

EFFECTS OF MOLECULAR ARCHITECTURE ON LIQUID CRYSTALLINE
THERMOSETS

By

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This work is dedicated to my family: my mother and father for their love, support, and advice; Jeong-a for her loving support, patience, and faith in me; and Benjamin who helps me keep my sanity by always greeting me with a smile and bringing unimagined joy into my life.

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EFFECTS OF MOLECULAR ARCHITECTURE ON LIQUID CRYSTALLINE THERMOSETS

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This work incorporates three studies on the influence of molecular architecture on liquid crystalline phase transitions, physical transformations, and thermal stability for acetylene functionalized liquid crystalline thermosets (LCTs). The first study focuses on synthesis and liquid crystalline phase characterization of acetylene functionalized LCTs. The second examines architecture's influence on liquid crystalline phase transitions and physical transformations that occur during isothermal curing of LCTs. The third deals with architecture and the thermal stability of the uncured and fully cured thermosets.

Two homologous series of LCT monomers, differing in mesogen length, were synthesized: with monomers composed of an aromatic mesogen based on either hydroquinone (nHQ) or biphenol (nBP), end-capped with acetylene functional groups, and terminated with flexible alkyl chains of 3 to 8 carbons in length. The nHQ monomers melt and clear at lower temperatures than the nBP series. The monomers were characterized with differential scanning calorimetry (DSC), dynamic thermogravimetric

analysis (TGA), and cross-polarized optical microscopy (POM). The monomers displayed liquid crystalline behavior similar to that of a related small molecule liquid crystal series. A related fully aromatic monomer was also synthesized (PEBP). It possesses higher melting and clearing temperatures, displays only a nematic phase, and has higher thermal stability.

The monomers of the two series were isothermally cured in a rheometer. Gelation times were determined from the shear moduli crossover point. Both series display an odd-even effect for gel times, even though the entire nHQ series is isotropic during the isothermal cure. This is the first time such behavior has been seen for an unordered system. From POM, the monomers lose their molecular ordering during initial chain extension, but may regain some order at later extents of curing if at low enough temperatures.

TGA and isothermal thermogravimetric analysis data were collected for cured PEBP in air and nitrogen atmospheres, from which activation energies were calculated. The data indicate independence with respect to atmosphere and thermal path taken to reach the first few percent of weight loss. The network is very stable, and shows 5% degradation at 491°C and 507°C, when tested at 10°C/min in air and nitrogen respectively.

CHAPTER 1 REVIEW OF LIQUID CRYSTALLINE MATERIALS AND TRANSFORMATION DIAGRAMS

Liquid Crystalline Materials

Liquid crystalline materials may exist as either small molecules or macromolecular materials. The small molecule materials have found some industrial applications, for example in flat panel displays. Macromolecular liquid crystals have found an industrial niche in the textile industry, for example with Kevlar®. Liquid crystalline polymers have many potential advantages over non-liquid crystalline polymers; for example: higher impact strengths, better barrier properties, and the ability to be oriented. Due to the potential applications for liquid crystalline materials, there have been many studies of small molecule liquid crystals, liquid crystalline polymers, and liquid crystalline thermosets. A brief review of these studies is presented below.

Liquid Crystalline Phases

The liquid crystalline state of some materials was discovered over 100 years ago in 1888. Typically, people are taught that materials exist in only three phases: solid, liquid, and gas. However, this is not the complete picture of the phases in which matter may exist. Some organic materials do not undergo a single transition from solid to liquid, but a series of transitions. These transitions are “mesomorphic phases,” meaning intermediate forms of phases.¹ The common name for such materials is a liquid crystal. This name arises from the fact that these materials have mechanical and symmetrical

properties that are intermediate between the crystal and liquid phases. For example, crystalline materials have the molecular centers of mass described as being on a three-dimensional lattice; in liquids, the centers of mass are not arranged in such an organized manner. De Gennes defines liquid crystals as materials that have long-range orientational ordering and either zero, one, or two-dimensional long-range positional ordering.¹ Isotropic liquids have zero-dimensional long-range positional order, and no long-range orientational order. Liquids with zero-dimensional long-range positional order that possess long-range orientational order are known as nematic, while liquids with one-dimensional long-range positional order and long-range orientational order are known as smectic. A schematic of these two types of liquid crystals is presented in Figure 1. The direction defined by $\hat{n}$ is known as the director. Molecules in nematic liquid crystals have long-range orientational ordering with respect to the director, but do not have long-range ordering with respect to intermolecular position. The smectic phase in Figure 1 has long-range orientational ordering with respect to its director, but also has long range positional ordering in one dimension. Since the positional ordering is in only one dimension, layers are formed; but there is no ordering within the layers. One type of liquid crystals, with two-dimensional positional order, is known as columnar or disc-like. Typically these molecules stack in packed columns; within the columns, the molecules are not packed in an ordered fashion.

One other related class of liquid crystals that will be mentioned briefly is cholesteric. Cholesteric liquid crystals are seen often as a combination of the nematic and smectic liquid crystal types. The reason is that cholesteric liquid crystals form layers.

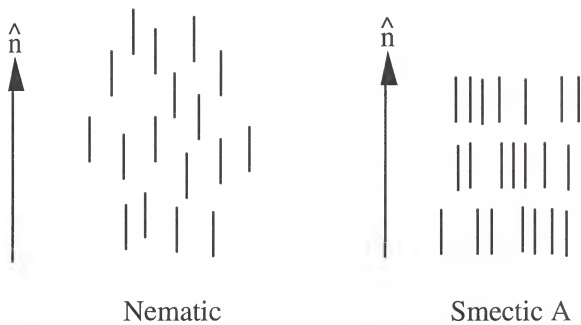


Figure 1. Schematics of the molecular packing of some calamitic liquid crystals.

However, each layer has its own director and the ordering within the layers is nematic-like. Often cholesteric liquid crystals are seen as twisted nematic liquid crystals. Because the molecules examined in this study are calamitic (rod-like) in shape and do not possess a chiral center, only nematic and smectic phases will be discussed.

There are two classifications of liquid crystals, lyotropic and thermotropic.

Lyotropic liquid crystals display liquid crystalline ordering upon reaching a critical concentration in a solvent, while thermotropic liquid crystals exhibit liquid crystallinity upon melting. The liquid crystalline thermosets (LCTs) synthesized for this study will be of the thermotropic type; and thus, that type will be discussed here. Thermotropic liquid crystals are known to progress through their phases, from most ordered to least ordered, with increasing temperature (i.e., crystalline to smectic to nematic to isotropic). Not all of the phases are present with all liquid crystals; as seen below, molecular architecture determines which phases are present for a material.

Small Molecule Liquid Crystals

Although there is currently no way to predict with certainty whether a given molecule will display liquid crystallinity, there are common structural features that allow some generalizations. For nematic and smectic liquid crystals, an elongated molecule is needed. These molecules are typically made from rigid rod-like segments, often with flexible tails. A schematic of a typical rigid rod liquid crystal molecule is shown in Figure 2. Flory² has mathematically predicted that the critical axial ratio (length-to-width ratio of the rod) is equal to approximately 6.4:1 for a thermotropic liquid crystal.

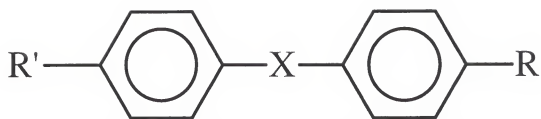


Figure 2. Molecular architecture of typical small molecule rigid rod liquid crystals.

This assumes that the only interaction between molecules is an insurmountable repulsive barrier upon contact. However, other interactions have been found to influence liquid crystallinity. The aromaticity of the benzene rings has been found to play a role in the stability of liquid crystals. Dewar et al.^{3,4} found that removal of the aromatic character of the rings, while keeping the shape constant, can still cause a decrease in the liquid crystalline phase stability as seen by a decrease in the clearing (isotropization) temperature. The study also found that rigidity was more important than the polar character of the mesogen (rigid rod group). While the group X may vary greatly, it needs to maintain the rigidity of the molecule. When the esters of the rigid 1,4-dihydroxybicyclooctane are compared to those of trans-1,4-dihydroxycyclohexane, the thermal stability of the nematic phase decreases by over 75°C.³ Also, the effect of non-planarity of the mesogen was examined. Twisting or kinking of the molecule will cause a destabilization of the mesophases due to interference in the packing.³ Another consideration for choosing the mesogenic unit deals with the cross-section of the molecule. The effects on the cross-section of the molecule from lateral substituents on the mesogenic group also have been explored.^{3,5-7} Lateral groups on the central ring have been found to disrupt the packing and side-to-side interaction of the molecules, thus destabilizing the liquid crystalline phase. Dewar⁴ found that areas that are narrower than the rest of the molecule also disrupt the liquid crystalline phases. Therefore, rod-shaped molecules with uniform cross-sections are preferred for liquid crystals.

The effect of the R and R' groups on the stability of the mesophases also has been examined.^{3,7-14} For a homologous series, extension of the alkyl chain leads to a decrease in the melting point and in the stability of the nematic mesophase. There are

two proposed reasons for these phenomena. The first reason is that the longer tails will act as a diluent, thus increasing the mean separation between molecules, reducing the interactions between the rod-like part of the molecules. The second reason is the reduction in the polarity of the tail. Because the larger mass will not have increased in polar character, the magnitude of the intermolecular interactions per unit area will have decreased. These effects are evident when two homologous series are synthesized that differ only in the tails; one using alkyl chains and the other using alkoxy chains with the same number of carbons. The mesophase of the alkoxy-tailed series is more stable.⁸

Another observation is that with increasing alkyl chain length the melting temperature will decrease, reach a minimum, and then slowly increase. At the same time, molecules with small alkyl chains might not exhibit a smectic phase, but the molecules with longer tails in the series might. Figure 3 is a plot of transition temperatures versus the number of carbons in the flexible alkoxy chain for a homologous series of 1,4-phenylene bis(4'-n-alkoxybenzoates) and illustrates these effects. One of the most interesting observations deals with what is known as the odd-even effect. This effect is typically seen in the nematic to isotropic (clearing) transition. When this transition is plotted for a homologous series, often two curves can be drawn: one for the odd number alkyl chain lengths and the other for the even ones. An example is shown in Figure 4. This effect is typically attributed to the differences in polarizability and conformational changes similar to those seen for the melting points of n-alkanes. This trend arises from the interactions of the terminal carbon in the chains. Boese et al. gave a complete description of how this phenomenon arises for the melting points of n-alkanes.¹⁵ The trend for the even curve being above the odd curve, as shown in Figure 4, is reversed for pure alkyl chains. It is

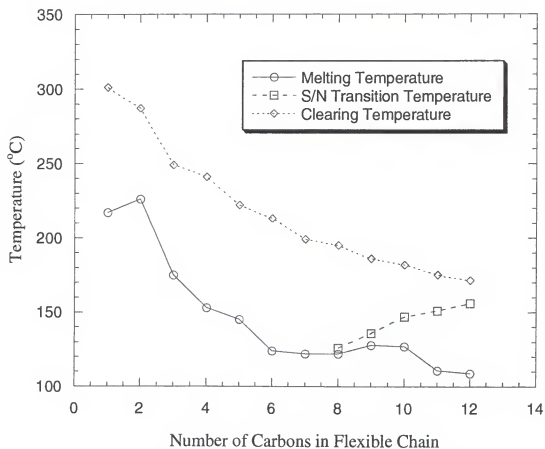


Figure 3. Plot for 1,4-phenylene bis(4'-n-alkoxybenzoates) of transition temperatures versus number of carbons in the alkoxy tail.¹⁴

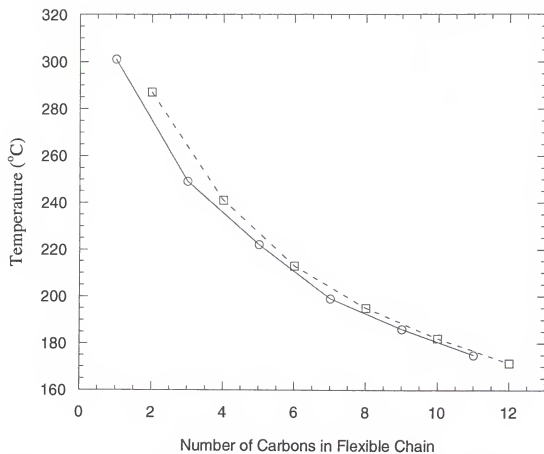


Figure 4. Plot for 1,4-phenylene bis(4'-n-alkoxybenzoates) of clearing temperatures versus number of carbons in the alkoxy tail, illustrating the odd-even effect.¹⁴

thought that the oxygen in the alkoxy group acts like a CH_2 , thus causing the two curves to be reversed. The smectic to nematic transition does not usually show this odd-even effect, and will converge with the clearing temperature at long chain lengths.

Liquid Crystalline Polymers (LCPs)

Liquid crystalline polymeric matrix materials are emerging as engineering resins because of their unique molecular arrangement. This unique arrangement has led to remarkable electrical and mechanical properties: for example, high tensile strength or unique electro-optical behavior.¹⁶ The liquid crystalline order found in these materials arises from rigid chain segments connected to other more flexible segments. These rigid segments may be incorporated in the polymer chain's backbone (main-chain liquid crystal polymer), as rigid side groups connected to a flexible chain (side-chain liquid crystal polymer), or in both. Often this rigid side group is decoupled through a flexible spacer to yield a greater orientational freedom.¹⁷ More extensive reviews of main-chain and side-chain liquid crystal polymers are available.¹⁷⁻¹⁹

Just like their small molecule liquid crystalline counterparts, LCPs can be classified into having either lyotropic or thermotropic behavior. Similar to nonliquid crystalline polymers, LCPs can also be either thermoplastics or thermosets. A large variety of LCP studies have been conducted.^{9,19-36} Due to their rigidity and anisotropy, liquid crystalline polymers have been found to have improved physical properties--some of which include high mechanical properties in the direction of orientation, excellent chemical and heat resistance, low thermal shrinkage, high dimensional stability, and low viscosity during processing--over related nonliquid crystalline polymers.

Many studies of LCPs have examined the effect of flexible spacer group length on the melting point and liquid crystalline transitions. In general, the melting temperature and clearing temperature have decreased with increasing spacer group length. Also, the smectic phases gain stability while the nematic phases lose stability with increasing spacer length. For example, when the flexible length is small, a crystal may melt to only a nematic phase. As the length is increased, the crystal may melt to a smectic phase and then transform to a nematic phase before isotropization. When the spacer length is large enough, the nematic phase may be nonexistent while the smectic phase remains. This effect is seen for spacers groups between rigid units and for alkyl end groups on mesogenic side chains. The effects from spacer length seen above are very similar to those found in small molecule liquid crystals. In fact, the odd-even effects mentioned in the previous section are also evident in polymeric liquid crystals. Although flexible spacer groups affect liquid crystal polymers in a fashion similar to that of small-molecule liquid crystals, LCPs also have a molecular weight effect. Molecular weight has an influence on LCP clearing temperatures similar to the T_g of the material. Initially, the clearing temperature rises nonlinearly with increasing chain molecular weight, and at a molecular weight of about 10,000, this behavior levels. This behavior is seen in both main-chain and side-chain LCPs; however, the molecular weight influence reaches a plateau at lower molecular weights for main-chain LCPs.

Interest in liquid crystalline thermosets (LCTs) arises from one of the main drawbacks of LCPs as matrix materials: poor mechanical properties in the transverse direction. The advantageous properties that LCTs are expected to possess are 1) high mechanical properties and chemical resistance; 2) low viscosity during processing;

allowing ease in filling molds of complex geometries; 3) better properties than LCPs when tested perpendicularly to the preferred direction; and 4) possibility to orient the molecules locally by action of electric or magnetic fields (and lock in the orientation upon curing).^{6,37-40} The high mechanical properties and chemical resistance arise due to the liquid crystalline order of the final material. The orientability and ability to fill complex molds is due to low viscosity of the uncured liquid crystalline monomers. Viscosities for typical small molecule nematic liquid crystals are on the order of 10^{-1} poise. The viscosity of water at room temperature is about 10^{-2} poise¹. For one example of a lyotropic liquid crystalline polymer solution (poly- γ -benzyl-L-glutamate; molecular weight: 150,000; concentrations ranging from ~12% to ~26%; steady shear rate of 10 sec^{-1}) the viscosity ranges from ~90 to ~20 poise.⁴¹ A poly(ethylene terephthalate/p-(acetoxybenzoic acid) blend (at 275°C) has viscosities ranging from about 20 to as high as 1000 poise depending on shear rate and p-(acetoxybenzoic acid) compositional percentage.³² Improved mechanical properties in the transverse direction are due to the network formed in thermosets, just as when nonliquid crystalline thermoplastics are compared to nonliquid crystalline thermosets. Su²⁷ presents an example of these advantages when an LCT is compared to a bisphenol A epoxy. The T_g of the LCT was 15.5% to 44% higher (depending on the curing agent used) and the coefficient of thermal expansion is reduced by 18.9%. In the same paper, Su also compares the electric properties of the materials to find that the LCT's dielectric strength is 13.7% greater and the dissipation factor is 14.2% less. Another advantage mentioned by Su and seen in other studies (LCTs and LCPs) is that the cure kinetics seem to be enhanced by the molecular ordering seen in liquid crystals. Comparison of LCT shrinkage during cure

with nonliquid crystalline systems shows a large difference. For example, Melissaris⁴² has found that upon solid-state polymerization of liquid crystalline di-*p*-ethynylbenzoyl esters the shrinkage was <3.2% while other nonliquid crystalline materials typically have larger shrinkage values (epoxies = ~8-9%, and acrylates = ~11-15%).

Similar to their nonliquid crystalline counterparts, LCTs can be formed with a variety of possible functional groups. Monomers with vinyl,⁴³ butadiene,³¹ acrylate and methacrylate,⁴⁴⁻⁴⁶ maleimide,^{28,47,48} nadimide,^{47,48} epoxy,^{24,27,37,49-53} and acetylene^{5,6,23,42,54-56} functional groups have been synthesized for use as LCTs.

Two general approaches have been taken in the formation of LCTs: either the monomers were liquid crystals, or the liquid crystalline order arose from initial products formed during curing (typically for epoxy LCTs, but also seen for nadimides).^{37,48,53} For monomers that are isothermally cured in an isotropic phase (either above the clearing temperature or with nonliquid crystalline monomers), liquid crystalline order may form during the cure. This is attributed to chain extension during cure, leading to larger aspect ratio and liquid crystallinity. There is also an example of an acetylene functionalized, liquid crystalline monomer isothermally cured in the isotropic phase that regains nematic liquid crystalline order, but then converts back to isotropic as curing continues. The initial conversion to nematic is attributed to chain extension, however, the conversion back to isotropic has not yet been completely explained.⁶

Acetylene functionalized compounds are well known resins that can be thermally cured (cure via an addition mechanism, thus without yielding a byproduct) and produce thermally stable networks with good mechanical properties. For these reasons, acetylene functionalized compounds are being developed to replace epoxies in hot, wet conditions.

Despite many reports of acetylene-based thermosets^{5,6,23,42,54-72} much is still unknown about these systems.

Although previous studies have examined some aspects of the effect molecular architecture has on liquid crystalline phase transitions during isothermal curing of LCTs, the influence of spacer group length has not been investigated. Also missing are studies examining how the physical transformations are affected by spacer length and liquid crystalline phase transitions that occur during isothermal curing.

Applications for Liquid Crystalline Materials

There are many applications of liquid crystalline materials. Liquid crystalline materials can find use in scientific, medical, technical, and structural applications.

Scientific application of liquid crystals is typically for use in physical chemistry or physics. Liquid crystals have found use as solvents to create ordered solutes that are not liquid crystals. The solute molecules have weak anisotropic interactions with the liquid crystalline matrix, and the guest orients appreciably toward the director axis. This orientation allows additional spectroscopic studies of the physical properties of the solutes to be determined. One example of these properties is the Van der Waals forces between the liquid crystalline matrix and the solute molecules. This can be determined from the value of the average axis of the solute compared to the optic axis of the matrix.⁷³

Medical uses of liquid crystalline materials vary widely. Because of the pitch in the cholesteric liquid crystals, different colors are seen for different conditions. One variable that affects the pitch is temperature. This allows the determination of temperature by observation of color. Cholesteric liquid crystals can be used in thermal

mapping of human skin for studies of the circulatory system, for diagnosis of circulatory diseases, and for detection of tumors. This is accomplished, for example, by placing a pad filled with a temperature-sensitive cholesteric liquid crystalline material.

Temperature variations due to reduced blood flow, rapid cancerous growth, or allergic reactions will be detectable when the pad is placed on the area of interest.

There are also various technical applications of liquid crystals. There are many different liquid crystalline displays. Cholesteric displays deal with thermal changes and have response times typically around 0.1 seconds. This restricts their use to displays where information changes slowly. Nematic liquid crystalline displays use electrodes to orient the liquid crystals, causing a change in the transmission properties for normal or polarized light. This change can require very little energy.

Liquid crystal polymers are finding use as structural materials. Kevlar, for example, has replaced steel, fiberglass, asbestos, and graphite in radial tires, armor plates, brake linings, and in composites. Kevlar has also found use in personal body armor.

Chemical and moisture resistances are very good for the Kevlar fibers.¹⁷ Liquid crystalline matrix materials are being explored for the aerospace industry. Aerospace requires lightweight materials that retain useful properties at 400°C and higher.⁷⁴

Weight-loss is an important indicator of thermal stability. The most commonly used method for comparing stabilities of experimental high-temperature polymers is dynamic thermogravimetric analysis (TGA). TGA data provides a threshold temperature at which major fragmentation occurs. This is an indication of the stability of the polymer structure. Another useful TGA experiment is known as isothermal thermogravimetric analysis (IGA). IGA allows determination of long-term stability at specific temperatures.

One drawback of this technique is that the material may show significant weight loss during the ramping up to the desired temperature. TGA and IGA are limited because they do not give data about any processes that do not include weight loss (softening or melting) nor data about the reactions and processes causing the weight loss. For thermosets, the former is not a serious limitation because most networks undergo irreversible decomposition before melting.⁷⁴ The potential advantages in properties of LCTs, stated previously, would apply well to these systems. Therefore, some of the monomers of this study have been designed for high temperature applications, specifically a fully aromatic monomer.

Measuring of Gelation and Vitrification

Gelation and vitrification occur during the curing of thermosetting materials. Gelation corresponds to the formation of an infinite network of crosslinked polymer molecules, while vitrification is defined as the point at which the T_g of the material is equal to the temperature at which the material is being examined. Vitrification marks the transformation from a rubber to a gelled glass if gelation has occurred. Identification of the gel point is important for the processing of thermosetting materials since it represents the highest conversion at which the material can still flow.⁷⁵

A variety of methods and criteria have been established for the determination of both gelation and vitrification. Differential scanning calorimetry (DSC), thermal mechanical analysis (TMA), torsional braid analysis (TBA), viscosimetry, rheometry, thermal scanning rheometry (TSR), and dynamic mechanical thermal analysis (DMTA) are a few of the techniques used to determine physical transformations of curing systems.⁷⁵⁻⁸² Although all of these methods have been used to construct transformation

diagrams, for historical and practical reasons only TBA and rheologically based techniques are reviewed below.

Many different criteria have been utilized to determine gel points. For rheological testing, multiple criteria have been established. Laza, et al.⁷⁷ cite four different criteria:

- 1) Criterion of maximum peak in $\tan\delta$, based on the point where there is a maximum difference between the elastic and viscous behaviour of the system.
- 2) Criterion corresponding to the crossover between the G' and G'' curves; at this point, the system presents not only an elastic but viscous behaviour as well, storing a similar amount of energy to the energy dissipated.
- 3) Criterion of the tangent line to the G' curve; this point corresponds to the crossing between the baseline ($G'=0$) and the tangent drawn at G' curve when G' reaches a value close to 100 KPa s.
- 4) Criterion of the viscosity; at this point the real dynamic viscosity η' reaches several determined values (1000, 2000, and 5000 Pa s).

Another example of gel point criteria used is by Hong and Chung.⁸² They measured the viscosity of vinyl ester resins at various temperatures with a steady shear rate of 9.3s^{-1} , and determined the gelation time “as the time when the viscosity increased very rapidly toward an infinite value.” For torsional braid analysis, gelation is determined from a peak in the logarithmic decrement curve.

Torsional Braid Analysis

Since its inception in 1962,⁸³ torsional braid analysis (TBA) has been used to determine gelation and vitrification points for use in thermosetting systems.⁸⁴⁻⁸⁸ TBA is a modified torsion pendulum in which a liquid thermosetting sample is impregnated into a heat cleaned, fiber braid (typically glass but other fibers have been used). A braid is used because braids do not have a torsional bias (clockwise or counter clockwise).

This technique has a high sensitivity because it is a resonance technique. The measurements are taken at the resonant frequency of the pendulum; this allows for resolution of minor transitions in the sample. Because of the anisotropy of the specimen, the organic matrix dominates the torsional rigidity rather than the filaments of the braid. A schematic of an automated torsional pendulum-TBA instrument is given in Figure 5. A typical experiment consists of a series of intermittently induced freely damped waves, whose frequency and damping change due to temperature, time, and either physical or chemical changes in the specimen. A light beam passes through a pair of polarizing lenses, one of which oscillates with the specimen. A photodetector detects the light that passes through the second polarizer, and an electrical signal is measured and plotted. A computer aligns the polarizers for a linear response, initiates oscillations, analyzes the damped waves, and provides a dynamic mechanical spectrum. The elastic shear modulus, G' , (expressed as relative rigidity) and the loss shear modulus, G'' , of a sample are related to the frequency (f) and the logarithmic decrement (Δ) of the oscillations by:

$$G' = Kf^2 \text{ and } G'' = G' \times \Delta/\pi$$

where K is a constant for an unchanging geometry, and $\Delta = (1/n)\ln(A_i/A_{i+n})$, with A_i and A_{i+n} equal to the amplitude of the i^{th} and $(i+n)^{\text{th}}$ oscillation in a damped wave. In practice, the measured frequency of a specimen changes from about 0.1 to 3 Hz during the transformation from liquid to glass. For the epoxy amine system used by Gillham,⁸⁹ a sample reaching its glass transition temperature (T_g) was found to have a damping frequency of ~0.7 Hz for a variety of curing temperatures. Data obtained from this

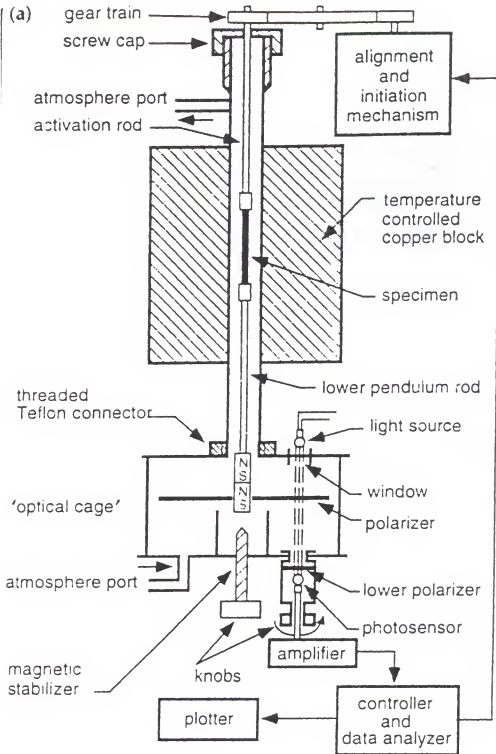


Figure 5. Schematic of an automated torsion pendulum-TBA instrument.⁸³

instrument and DSC data have enabled cure kinetics studies and construction of time-temperature-transformation (TTT) and continuous heating transformation (CHT) diagrams.⁸⁴⁻⁹⁶

While torsional braid analysis may allow convenient determination of the gelation and vitrification points for thermosetting systems, which often have viscosities so low that other traditional means of dynamic mechanical analysis are unable to measure them, TBA requires the use of a high modulus substrate. This has two disadvantages. The first disadvantage is the loss of ability to receive accurate values for the storage and loss moduli of the thermosetting resin. The second disadvantage is the possibility of the signal for modulus changes in the resin being lost in the much larger elastic modulus of the substrate if a perfect braid is not used. The TBA is also a very specialized instrument, which does not have applications to other systems.

Rheological Techniques and Gelation Criteria

More recently, rheological techniques have been developed and used to determine gelation and vitrification.^{75,77-81} These studies mostly used a variety of geometries including cone and plate⁷⁸ and parallel plate^{75,79-81} geometries. Gelation and vitrification times for low to moderate viscosity curing systems were determined using oscillatory shearing of the samples and the gelation time criteria mentioned previously.

There are a few advantages in using a rheometer rather than a torsional braid analyzer to determine physical transformation. First, new specialized equipment does not need to be purchased. Second, sample preparation and loading is simplified. Third, initial sample viscosities may range from the very low to moderately high and still be tested. For these reasons, rheology was used for this study.

Transition Diagrams for Thermosets

Nonequilibrium phase diagrams,^{5,6,48} liquid crystalline phase time-temperature-phase transformation diagrams,⁵³ and process characterization diagrams⁵⁰ for LCTs have been theorized and experimentally constructed. The nonequilibrium phase diagrams illustrate the liquid crystalline phases for a LCT. These phases are noted on a plot of isothermal cure temperature versus the extent of reaction. The physical phases noted are only that of liquid and solid, and does not include information about the gel times. The liquid crystalline phase time-temperature-phase transformation diagram yields similar data to that of the nonequilibrium phase diagram, but yields no data about the physical phase of the material. Liquid crystalline phase time-temperature-phase transformation diagrams plot the cure temperature versus time rather than extent of reaction. The process characterization diagram is not a phase diagram and does not allow prediction of isothermal cure profiles that have not already been tested for the LCT. While the diagram looks similar to the nonequilibrium diagram, the process characterization diagram does not give any physical phase data.

Two studies^{6,48} describe the experimental behavior of the material by qualitatively relating the phase seen at a given temperature with the extent of cure for the material. An example of such a diagram is given in Figure 6. As seen in the figure, a liquid crystalline material may be cured in the isotropic phase and regain the liquid crystalline ordering in the solid. This conversion back to the liquid crystalline phase during cure has been ascribed to chain extension reactions. These longer chains have a

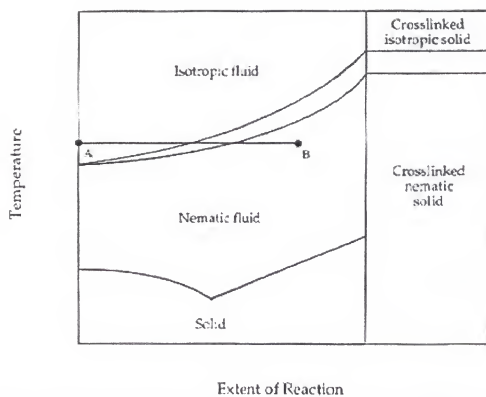


Figure 6. Nonequilibrium phase diagram describing the behavior of liquid-crystal thermosets.⁴⁸

higher length to diameter ratio, leading to a higher isotropization temperature than the monomers. The emergence of liquid crystalline order during cure has been seen in epoxies,⁵³ bisacetylenes,⁶ bisnadimides,⁴⁸ and bis(methylnadimide)s.⁴⁸ The time-temperature-phase transformation diagram of Lin et al. reports the liquid crystalline phase, and the time to reach that phase, for an isothermal curing profile of a liquid crystalline epoxy. In that diagram, the S-curve represents the time the material must cure to reach the critical chain length for liquid crystallinity by chain extension. Another experimentally determined transformation diagram, relating transformation temperature with cure time for an isothermal cure,⁵ is shown in Figure 7. The major disadvantage of the type of transformation diagram seen in Figure 7 is that the diagram is based on one cure temperature. This means that predictions of the physical phases (or liquid crystalline phases) of the material for different cure temperatures cannot be made. A time-temperature-physical transformation (TTT) diagram allows the prediction of a material's physical phase for many different isothermal cure profiles, and is a powerful tool for determining processing conditions.

TTT diagrams, shown in Figure 8, are constructed to relate the time to a transformation, such as liquid crystalline phase changes, gelation, or vitrification, to the isothermal cure temperature. Under non-isothermal cure conditions, the material can undergo various changes similar to those encountered in an isothermal cure. Continuous heating transformation (CHT) diagrams can be constructed to display times and temperatures these events occur for various heating rates.⁸⁴ An example of a CHT diagram is presented in Figure 9. The S-shaped line in both figures represents the

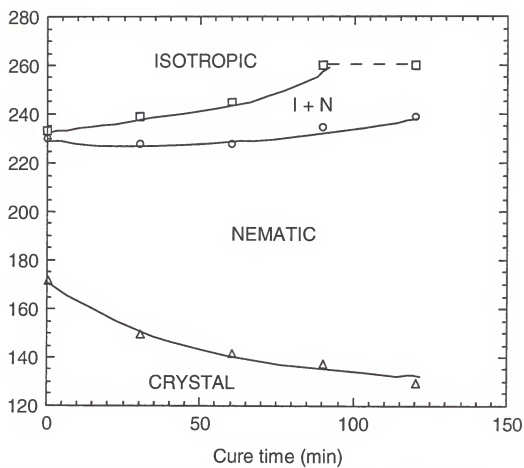


Figure 7. Experimentally determined transformation diagram for a 200°C isothermal cure cycle.⁵

TTT CURE DIAGRAM ISO-CONVERSION CONTOURS

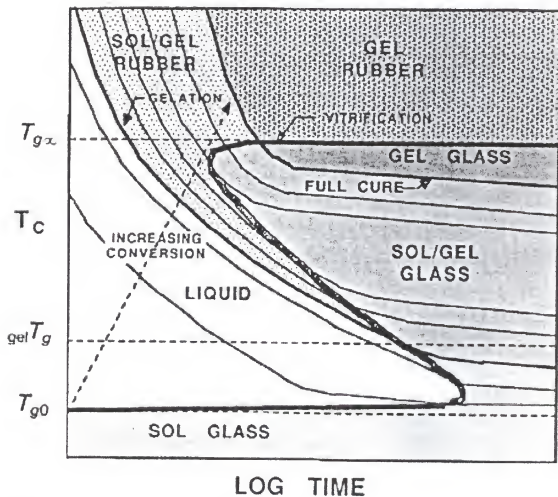


Figure 8. TTT diagram for a thermosetting material.⁹³

**CHT DIAGRAM FOR DER332/TMA8:
TEMPERATURE AND T_g VS. LOG TIME AT DIFFERENT HEATING RATES**

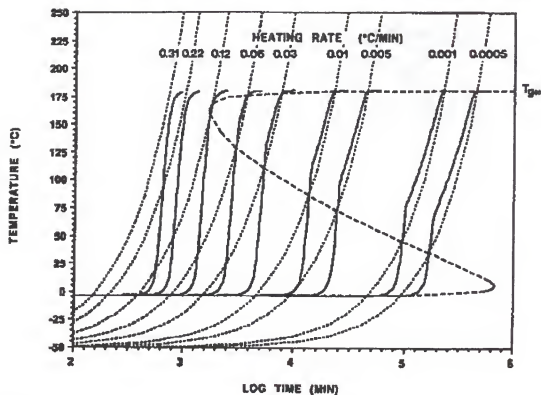


Figure 9. CHT diagram for a thermosetting material.⁸⁴

devitrification-vitrification-devitrification contour calculated from curing epoxy samples in a TBA. Many studies of thermosetting systems have calculated physical transformation TTT^{24,76,78,82,85,89,93-95} or CHT^{24,84,85,89,93} diagrams to help explain the physical transformations the curing system undergoes during a cure profile. Lin et al.⁵³ constructed TTT diagrams for the curing of a liquid crystalline epoxy with two different hardeners. In their diagrams, times to liquid crystalline transformations were described, rather than physical changes, during the isothermal curing.

As stated previously, the time to gelation is a very important factor for the isothermal processing of a thermosetting material, however, for LCTs the liquid crystalline phases are also affected by time during an isothermal cure. One goal of this study is the creation of a new TTT diagram for liquid crystalline thermosets. This new diagram will allow determination of both the liquid crystalline phase transition times and physical transformation times for an isothermal cure temperature. This new TTT diagram will allow the investigation into the affect molecular architecture has on the physical and liquid crystalline phases of isothermally curing acetylene functionalized LCTs.

Goals of This Study

This study focuses on the effects molecular structure has on physical transformations and liquid crystalline phases for acetylene functionalized LCTs. The study consists of three main goals. The first is the synthesis of two homologous series of acetylene functionalized LCT monomers, which are liquid crystals before curing, to determine how molecular architecture affects the liquid crystalline phase transitions for the uncured monomers. To achieve this goal the monomers are characterized using

cross-polarized optical microscopy, DSC, and TGA. The second goal deals with effects of molecular architecture on the physical transformations and liquid crystalline phases during isothermal curing. The gelation times and liquid crystalline phases are determined using parallel plate rheology and cross-polarized optical microscopy. The final goal deals with the thermal stability of a related fully aromatic LCT monomer. This monomer was synthesized to yield a network that both retains the liquid crystalline order, and shows high thermal stability. The monomer and cured material were characterized with cross-polarized optical microscopy and DSC to determine the liquid crystalline phases. Both dynamic and isothermal TGA experiments were conducted to determine the thermal stability of the final network. This study elucidates the effects caused by changes in molecular architecture of acetylene functionalized liquid crystalline thermoset monomers. This is accomplished through the construction of TTT diagrams, which include both physical and liquid crystalline transformations, of two homologous series of monomers. Comparison of TGA data allows determination of the affect of molecular architecture on thermal stability.

CHAPTER 2

SYNTHESIS AND PHASE BEHAVIOR OF ACETYLENE FUNCTIONALIZED LIQUID CRYSTALLINE THERMOSET MONOMERS

Introduction

The demand for polymeric matrix materials for composites has increased over the past half a century. Industries such as aviation, space exploration, shipbuilding, automotive manufacturing and machine building are all starting to demand more from polymer matrix composites. In order for polymers to meet the new requirements as technology advances, new polymers, and a better understanding of structure-property relationships, are needed. The high strength to weight ratio for polymers has made them attractive for planes and automobiles.^{97,98} Liquid crystalline polymeric matrix materials are emerging as engineering resins due to their unique molecular arrangement. This unique arrangement has led to remarkable mechanical properties.¹⁶ Similar to their non-liquid crystalline counterparts, LCTs can be formed with a variety of possible functional groups. Monomers with vinyl,⁴³ butadiene,³¹ acrylate and methacrylate,⁴⁴⁻⁴⁶ maleimide,^{28,47,48} nadimide,^{47,48} epoxy,^{24,27,37,49-53} and acetylene^{5,6,23,42,54-56} functional groups have been synthesized for use as LCTs. Advantages of acetylene monomers are that they can be thermally cured without a byproduct and do not require a second species for polymerization.

While there have been many reports of acetylene based thermosets ^{5,6,23,42,54-72} there is still very much which is unknown about these systems, especially for liquid

crystalline thermosets. This chapter deals with the synthesis of two homologous series of novel acetylene functionalized LCT monomers, and investigates the effects of molecular architecture on the liquid crystalline phase transitions. The synthetic scheme for these monomers is presented in Figure 10. These monomers are similar to ones reported previously by Douglas et al.⁶ However, while their main interest was in the effects of the central mesogen on liquid crystalline phase behavior, the focus of this study is on the phase behavior due to changes in the length of a flexible end group.

Experimental Section

Materials

All chemicals were used as received. Methyl-4-iodobenzoate, bis-(triphenylphosphine)- palladium(II)chloride, triphenylphosphine, copper(I)iodide (98%), triethylamine, oxalyl chloride, sodium hydroxide, concentrated hydrochloric acid, diethylether, dimethylformamide, methanol, benzene, 1-pentyne (99%), 1-octyne (99%), and biphenol (97%) were all received from Acros. The hydroquinone (99%), 1-hexyne (97%), 1-heptyne (98%), 1-nonyne (99%), and 1-decyne (98%) were received from Aldrich.

General Procedures

Elemental analyses were determined at the Chemistry Department at the University of Florida. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) were recorded on a Gemini-300 instrument in CDCl₃ using TMS as an internal standard.

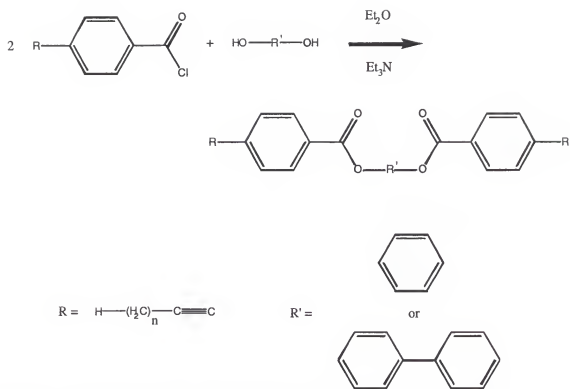


Figure 10. Synthesis of bisethynyl functionalized monomers with flexible tails.

Synthesis

All of the monomers were synthesized in a similar manner. The nomenclature used for the monomers consists of a number, representing the number of carbons in the flexible chain, followed by either HQ or BP, identifying whether hydroquinone or biphenol were used as the central unit of the mesogen. The synthesis of the 6BP monomer will be illustrated as an example. NMR spectra for these compounds may be found in Appendix A.

p-(1-octynyl)benzoic acid (6acid)

To a heat/vacuum dried and argon flushed 500 mL 3-neck flask with stir-bar, methyl-4-iodobenzoate (25.7959 g, .098 mol), octyne (22.4 mL, 16.231 g, .147 mol), triethylamine (250 mL, 181.50 g, 1.794 mol), triphenyl phosphine (0.1046 g, .3.98 mmol), bis(triphenyl phosphine)Palladium (II) chloride (0.0979 g, .139 mmol), and copper iodide (0.0666 g, .3.5 mmol), were added and stirred in an argon atmosphere. The light yellow slurry was stirred under argon for 48 hours at room temperature. [Note: Times and temperatures varied for different compounds. See specific compound below for details]. The solution was then filtered, and the solid was washed with diethyl ether until light gray or white in color. The yellow filtrate was then reduced under vacuum. The filtrate was then diluted with hexanes and thrice stirred with n-alumina gel for two hours. The alumina gel slurry was filtered and washed with hexanes each time. The filtrate was then reduced under vacuum at room temperature to remove the hexanes. The light yellow liquid was then refluxed with sodium hydroxide (10.8 g, .270 mol), water (128 mL), and methanol (140 mL) for 20 hours. [For alkynes with shorter chains, the methyl-4-(1-alkynyl)benzoate is a crystal with a melting temperature near room

temperature]. The orange liquid was then allowed to cool to room temperature. The solution was then acidified with 37% HCl. A yellow/beige solid formed upon acidification. The solid was then recrystallized twice from hexanes and dried in a vacuum oven at 60 °C for 24 hours to yield 15.3202 g (68%) of 6acid. EA: Theory: 78.23% C, 7.88% H, 13.89% O; Actual: 78.52% C, 8.00% H. 300 MHz ^1H -NMR (CDCl_3): δ = .89 (t, 3 H, $-\text{CH}_3$), 1.4 (m, 6 H, $-\text{CH}_2-$), 1.6 (m, 2 H, $-\text{CH}_2-$), 2.4 (t, 2 H, $-\text{CH}_2-$), 7.4 (d, 2 H, aromatic), 8.0 (d, 2 H, aromatic). 75 MHz ^{13}C -NMR (CDCl_3): δ = 14.0 ($-\text{CH}_3$), 19.5 ($-\text{CH}_2-$), 22.6 ($-\text{CH}_2-$), 28.5 ($-\text{CH}_2-$), 28.6 ($-\text{CH}_2-$), 31.3 ($-\text{CH}_2-$), 80.1 (acetylene), 94.7 (acetylene), 127.9, 130.0, 131.6 (aromatic), 171.8 ($-\text{COO}-$).

***p*-(1-pentynyl)benzoic acid (3acid)**

Yield 4.19 g (45.5%). EA: Theory: 76.57% C, 6.43% H, 17.00% O; Actual: 76.44% C, 6.71% H. 300 MHz ^1H -NMR (CDCl_3): δ = 1.0 (t, 3 H, $-\text{CH}_3$), 1.6 (m, 2 H, $-\text{CH}_2-$), 2.4 (t, 2 H, $-\text{CH}_2-$), 7.5 (d, 2 H, aromatic), 8.0 (d, 2 H, aromatic). 75 MHz ^{13}C -NMR (CDCl_3): δ = 13.5 ($-\text{CH}_3$), 21.5 ($-\text{CH}_2-$), 22.0 ($-\text{CH}_2-$), 80.2 (acetylene), 94.4 (acetylene), 127.9, 129.9, 130.0, 131.5 (aromatic), 172.0 ($-\text{COO}-$).

***p*-(1-hexynyl)benzoic acid (4acid)**

Yield 16.2728 g (78%). EA: Theory: 77.20% C, 6.98% H, 15.82% O; Actual: 77.35% C, 7.33% H. 300 MHz ^1H -NMR (CDCl_3): δ = .94 (t, 3 H, $-\text{CH}_3$), 1.4 (m, 2 H, $-\text{CH}_2-$), 1.6 (m, 2 H, $-\text{CH}_2-$), 2.4 (t, 2 H, CH_2), 7.4 (d, 2 H, aromatic), 8.0 (d, 2 H, aromatic). 75 MHz ^{13}C -NMR (CDCl_3): δ = 13.6 ($-\text{CH}_3$), 19.2 ($-\text{CH}_2-$), 22.0 ($-\text{CH}_2-$), 30.6 ($-\text{CH}_2-$), 80.1 (acetylene), 94.6 (acetylene), 127.9, 130.0, 131.6, (aromatic), 171.9 ($-\text{COO}-$).

***p*-(1-heptynyl)benzoic acid (5acid)**

Yield 14.5425 g (68%). EA: Theory: 77.75% C, 7.46% H, 14.80% O; Actual: 77.49% C, 8.33% H. 300 MHz $^1\text{H-NMR}$ (CDCl_3): δ = .91 (t, 3 H, $-\text{CH}_3$), 1.4 (m, 4 H, $-\text{CH}_2-$), 1.6 (m, 2 H, $-\text{CH}_2-$), 2.4 (t, 2 H, $-\text{CH}_2-$), 7.4 (d, 2 H, aromatic), 8.0 (d, 2 H, aromatic). 75 MHz $^{13}\text{C-NMR}$ (CDCl_3): δ = 14.0 ($-\text{CH}_3$), 19.5 ($-\text{CH}_2-$), 22.2 ($-\text{CH}_2-$), 28.3 ($-\text{CH}_2-$), 31.1 ($-\text{CH}_2-$), 80.0 (acetylene), 94.7 (acetylene), 127.9, 130.0, 131.5 (aromatic), 172.0 ($-\text{COO}-$).

***p*-(1-nonyl)benzoic acid (7acid)**

The initial light yellow slurry was stirred under argon for 16 hours at 80 °C. Yield 16.6479 g (70%) of 7acid. EA: Theory: 78.65% C, 8.25% H, 13.10% O; Actual: 78.40% C, 8.37% H. 300 MHz $^1\text{H-NMR}$ (CDCl_3): δ = .88 (t, 3 H, $-\text{CH}_3$), 1.3 (m, 8 H, $-\text{CH}_2-$), 1.6 (m, 2 H, $-\text{CH}_2-$), 2.4 (t, 2 H, $-\text{CH}_2-$), 7.4 (d, 2 H, aromatic), 8.0 (d, 2 H, aromatic).

***p*-(1-decynyl)benzoic acid (8acid)**

The initial light yellow slurry was stirred under argon for 46 hours at 80 °C. Yield 7.0044 g (26.26%) of 8acid. EA: Theory: 79.03% C, 8.58% H, 12.39% O; Actual: 79.36% C, 8.73% H. 300 MHz $^1\text{H-NMR}$ (CDCl_3): δ = .87 (t, 3 H, $-\text{CH}_3$), 1.4 (m, 10 H, $-\text{CH}_2-$), 1.6 (m, 2 H, $-\text{CH}_2-$), 2.4 (t, 2 H, $-\text{CH}_2-$), 7.4 (d, 2 H, aromatic), 8.0 (d, 2 H, aromatic). 75 MHz $^{13}\text{C-NMR}$ (CDCl_3): δ = 14.1 ($-\text{CH}_3$), 19.5 ($-\text{CH}_2-$), 22.7 ($-\text{CH}_2-$), 28.5 ($-\text{CH}_2-$), 28.9 ($-\text{CH}_2-$), 29.1 ($-\text{CH}_2-$), 29.2 ($-\text{CH}_2-$), 31.8 ($-\text{CH}_2-$), 80.1 (acetylene), 94.7 (acetylene), 127.9, 130.0, 131.5 (aromatic), 172.0 ($-\text{COO}-$).

6BP Monomer

To a heat/vacuum dried and argon flushed 500 mL 3-neck flask with stir-bar *p*-(1-octynyl)benzoic acid (8.95 g, 0.0389 mol) was added to benzene (60 mL) and stirred in an argon atmosphere. Oxalyl chloride 98% (5.995 g, 8.9 mL, 0.047 mol) was slowly added with stirring. The solution was then heated to reflux. The bright yellow solution was stirred at reflux for 3.5 hours and then allowed to cool to room temperature. The remaining benzene and oxalyl chloride were then removed via vacuum. The resulting (*p*-(1-octynyl)benzoyl chloride) was used immediately. Biphenol (1.3629 g, 0.0073 mol), diethyl ether (50 mL), and triethylamine (1.89 g, 2.6 mL, 0.019 mol) were stirred in an ice bath for 30 minutes. The freshly synthesized *p*-(1-octynyl)benzoyl chloride (4.6 mL, 0.0184 mol) was then slowly added. The slurry was then allowed to warm to room temperature and stir for 3.5 hours. The volatiles were then removed via vacuum. Warm water (110 mL) was then added, and the resulting slurry was centrifuged and decanted. The solid was recrystallized from acetone and dried in a vacuum oven at 60 °C for 24 hours to yield 4.4564 g (68%) of 6BP. EA: Theory: 82.59% C, 6.93% H, 10.48% O; Actual: 82.52% C, 7.18% H. 300 MHz ¹H-NMR (CDCl₃): δ = .90 (t, 6 H, -CH₃), 1.4 (m, 12 H, -CH₂-), 1.6 (m, 4 H, -CH₂-), 2.4 (t, 4 H, -CH₂-), 7.3 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 7.6 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). 75 MHz ¹³C-NMR (CDCl₃): δ = 14.0 (-CH₃), 19.6 (-CH₂-), 22.5 (-CH₂-), 28.5 (-CH₂-), 28.6 (-CH₂-), 31.3 (-CH₂-), 80.1 (acetylene), 94.7 (acetylene), 122.0, 128.0, 128.2, 129.8, 130.0, 131.6, 138.2, 150.4 (aromatic), 164.8 (-COO-).

3BP Monomer

Recrystallized from DMAC/water. EA: Theory: 82.11% C, 5.74% H, 12.15% O; Actual: 81.85% C, 5.51% H. 300 MHz ^1H -NMR (CDCl_3): δ = 1.1 (t, 6 H, $-\text{CH}_3$), 1.6 (m, 4 H, $-\text{CH}_2-$), 2.4 (m, 4 H, $-\text{CH}_2-$), 7.3 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 7.6 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). 75 MHz ^{13}C -NMR (CDCl_3): δ = 13.6 ($-\text{CH}_3$), 21.5 ($-\text{CH}_2-$), 22.1 ($-\text{CH}_2-$), 80.2 (acetylene), 94.5 (acetylene), 122.0, 128.2, 129.7, 130.0, 131.6, 138.2, 150.4 (aromatic), 164.7 ($-\text{COO}-$).

4BP Monomer

Recrystallized from DMF/water. EA: Theory: 82.28% C, 6.18% H, 11.54% O; Actual: 82.61% C, 6.45% H. 300 MHz ^1H -NMR (CDCl_3): δ = .96 (t, 6 H, $-\text{CH}_3$), 1.5 (m, 8 H, $-\text{CH}_2-$), 2.4 (t, 4 H, $-\text{CH}_2-$), 7.3 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 7.6 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). 75 MHz ^{13}C -NMR (CDCl_3): δ = 13.6 ($-\text{CH}_3$), 19.2 ($-\text{CH}_2-$), 22.0 ($-\text{CH}_2-$), 30.6 ($-\text{CH}_2-$), 80.1 (acetylene), 94.6 (acetylene), 122.0, 128.0, 128.2, 129.8, 130.0, 131.6, 138.2, 150.4 (aromatic), 164.7 ($-\text{COO}-$).

5BP Monomer

EA: Theory: 82.44% C, 6.57% H, 10.98% O; Actual: 82.29% C, 6.51% H. 300 MHz ^1H -NMR (CDCl_3): δ = .93 (t, 6 H, $-\text{CH}_3$), 1.4 (m, 8 H, $-\text{CH}_2-$), 1.6 (m, 4 H, $-\text{CH}_2-$), 2.4 (t, 4 H, $-\text{CH}_2-$), 7.3 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 7.6 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). 75 MHz ^{13}C -NMR (CDCl_3): δ = 14.0 ($-\text{CH}_3$), 19.5 ($-\text{CH}_2-$), 22.2 ($-\text{CH}_2-$), 28.3 ($-\text{CH}_2-$), 31.1 ($-\text{CH}_2-$), 80.1 (acetylene), 94.7 (acetylene), 122.0, 128.1, 128.2, 129.8, 130.0, 131.6, 138.2, 150.4 (aromatic), 164.8 ($-\text{COO}-$).

7BP Monomer

EA: Theory: 82.72% C, 7.26% H, 10.02% O; Actual: 83.19% C, 7.30% H. 300 MHz $^1\text{H-NMR}$ (CDCl_3): δ = .91 (t, 6 H, $-\text{CH}_3$), 1.3 (m, 12 H, $-\text{CH}_2-$), 1.5 (m, 4 H, $-\text{CH}_2-$), 1.6 (m, 4 H, $-\text{CH}_2-$), 2.4 (t, 4 H, $-\text{CH}_2-$), 7.3 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 7.6 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). 75 MHz $^{13}\text{C-NMR}$ (CDCl_3): δ = 14.1 ($-\text{CH}_3$), 19.6 ($-\text{CH}_2-$), 22.6 ($-\text{CH}_2-$), 28.6 ($-\text{CH}_2-$), 28.8 ($-\text{CH}_2-$), 28.9 ($-\text{CH}_2-$), 31.7 ($-\text{CH}_2-$), 80.1 (acetylene), 94.7 (acetylene), 122.0, 128.0, 128.2, 129.7, 130.0, 131.6, 138.2, 150.3 (aromatic), 164.8 ($-\text{COO}-$).

8BP Monomer

EA: Theory: 82.85% C, 7.56% H, 9.60% O; Actual: 82.82% C, 7.67% H. 300 MHz $^1\text{H-NMR}$ (CDCl_3): δ = .88 (t, 6 H, $-\text{CH}_3$), 1.4 (m, 20 H, $-\text{CH}_2-$), 1.6 (m, 4 H, $-\text{CH}_2-$), 2.4 (t, 4 H, $-\text{CH}_2-$), 7.3 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 7.6 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). [Due to low solubility, a carbon NMR was not recorded]

Note: For the hydroquinone-derived monomers, the same procedure was followed, however, biphenol was replaced with the molar equivalent of hydroquinone and the final monomer was recrystallized from DMF/water.

3HQ Monomer

EA: Theory: 79.98% C, 5.82% H, 14.21% O; Actual: 80.01% C, 5.92% H. 300 MHz $^1\text{H-NMR}$ (CDCl_3): δ = 1.1 (t, 6 H, $-\text{CH}_3$), 1.6 (m, 4 H, $-\text{CH}_2-$), 2.4 (m, 4 H, $-\text{CH}_2-$), 7.2 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 7.6 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). [Due to low solubility, a carbon NMR was not recorded]

4HQ Monomer

EA: Theory: 80.31% C, 6.32% H, 13.37% O; Actual: 80.33% C, 6.63% H, 10.30% O. 300 MHz ^1H -NMR (CDCl_3): δ = .95 (t, 6 H, $-\text{CH}_3$), 1.5 (m, 4 H, $-\text{CH}_2-$), 1.6 (m, 4 H, $-\text{CH}_2-$), 2.4 (t, 4 H, $-\text{CH}_2-$), 7.3 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). 75 MHz ^{13}C -NMR (CDCl_3): δ = 13.6 ($-\text{CH}_3$), 19.2 ($-\text{CH}_2-$), 22.0 ($-\text{CH}_2-$), 30.6 ($-\text{CH}_2-$), 80.1 (acetylene), 94.6 (acetylene), 122.6, 127.9, 129.8, 130.0, 131.6, 148.3 (aromatic), 164.6 ($-\text{COO}-$).

5HQ Monomer

EA: Theory: 80.60% C, 6.77% H, 12.63% O; Actual: 80.53% C, 7.0% H. 300 MHz ^1H -NMR (CDCl_3): δ = .92 (t, 6 H, $-\text{CH}_3$), 1.4 (m, 8 H, $-\text{CH}_2-$), 1.6 (m, 4 H, $-\text{CH}_2-$), 2.4 (t, 4 H, $-\text{CH}_2-$), 7.3 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). 75 MHz ^{13}C -NMR (CDCl_3): δ = 14.0 ($-\text{CH}_3$), 19.5 ($-\text{CH}_2-$), 22.2 ($-\text{CH}_2-$), 28.3 ($-\text{CH}_2-$), 31.1 ($-\text{CH}_2-$), 80.1 (acetylene), 94.7 (acetylene), 122.6, 127.9, 129.8, 130.0, 131.6, 148.4 (aromatic), 164.6 ($-\text{COO}-$).

6HQ Monomer

EA: Theory: 80.56% C, 7.51% H, 11.92% O; Actual: 80.67% C, 7.35% H. 300 MHz ^1H -NMR (CDCl_3): δ = .90 (t, 6 H, $-\text{CH}_3$), 1.4 (m, 12 H, $-\text{CH}_2-$), 1.6 (m, 4 H, $-\text{CH}_2-$), 2.4 (t, 4 H, $-\text{CH}_2-$), 7.3 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). 75 MHz ^{13}C -NMR (CDCl_3): δ = 14.1 ($-\text{CH}_3$), 19.6 ($-\text{CH}_2-$), 22.6 ($-\text{CH}_2-$), 28.5 ($-\text{CH}_2-$), 28.6 ($-\text{CH}_2-$), 31.3 ($-\text{CH}_2-$), 80.0 (acetylene), 94.7 (acetylene), 122.6, 127.9, 129.8, 130.0, 131.6, 148.3, (aromatic), 164.6 ($-\text{COO}-$).

7HQ Monomer

EA: Theory: 80.82% C, 7.85% H, 11.33% O; Actual: 81.60% C, 7.59% H, 10.30% O. 300 MHz ^1H -NMR (CDCl_3): δ = .90 (t, 6 H, $-\text{CH}_3$), 1.3 (m, 12 H, $-\text{CH}_2-$), 1.4 (m, 4 H, $-\text{CH}_2-$), 1.6 (m, 4 H, $-\text{CH}_2-$), 2.4 (t, 4 H, $-\text{CH}_2-$), 7.3 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). 75 MHz ^{13}C -NMR (CDCl_3): δ = 14.1 ($-\text{CH}_3$), 19.6 ($-\text{CH}_2-$), 22.6 ($-\text{CH}_2-$), 28.6 ($-\text{CH}_2-$), 28.8 ($-\text{CH}_2-$), 28.9 ($-\text{CH}_2-$), 31.7 ($-\text{CH}_2-$), 80.0 (acetylene), 94.7 (acetylene), 122.6, 127.9, 129.8, 130.0, 131.6, 148.3, (aromatic), 164.6 ($-\text{COO}-$).

8HQ Monomer

EA: Theory: 81.32% C, 7.85% H, 10.83% O; Actual: 81.67% C, 8.12% H. 300 MHz ^1H -NMR (CDCl_3): δ = .88 (t, 6 H, $-\text{CH}_3$), 1.4 (m, 20 H, $-\text{CH}_2-$), 1.6 (m, 4 H, $-\text{CH}_2-$), 2.4 (t, 4 H, $-\text{CH}_2-$), 7.3 (d, 4 H, aromatic), 7.5 (d, 4 H, aromatic), 8.1 (d, 4 H, aromatic). 75 MHz ^{13}C -NMR (CDCl_3): δ = 14.1 ($-\text{CH}_3$), 19.5 ($-\text{CH}_2-$), 22.6 ($-\text{CH}_2-$), 28.5 ($-\text{CH}_2-$), 28.9 ($-\text{CH}_2-$), 29.1 ($-\text{CH}_2-$), 29.2 ($-\text{CH}_2-$), 31.8 ($-\text{CH}_2-$), 80.1 (acetylene), 94.7 (acetylene), 122.6, 128.0, 129.8, 130.0, 131.6, 148.3 (aromatic), 164.6 ($-\text{COO}-$).

Cross-Polarized Optical Microscopy (POM)

POM experiments were conducted using a Nikon Fluorophot microscope and a Linkham Scientific Instruments HFS91 hot stage controlled by a TMS 91 temperature controller. Small amounts of the monomers were placed between two 12 mm round, glass microscope cover slips and observed between crossed polarizers. The sample was heated at a rate of $10^\circ\text{C}/\text{minute}$ to 400°C . The liquid crystalline transition temperatures and phases were determined by optical texture.

Thermal Analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a Seiko Instruments SSC5200 TG/DTA 320 and SSC5200 DSC220C, respectively, with an SDM5600H Data Station. Samples of 5-10 mg were used. The TGA experiments were carried out in streams of air over the temperature range of 25°C to 1000°C. The heating rate used was 10°C/min. The melting point and liquid crystalline transitions for the uncured monomers were determined from the extrapolated onsets of peaks in DSC experiments while in a nitrogen gas flow with a heating rate of 10°C/min. All thermal transitions were confirmed using POM.

Results and Discussion

Monomer Synthesis

Twelve new acetylene functionalized liquid crystalline monomers have been synthesized. None of these monomers have been reported previously. These monomers are mesogenic units functionalized on both ends with acetylene units, and terminated with flexible alkyl chains of lengths from 3 to 8 carbons. Compounds with similar molecular structure have been reported previously; however, in those studies the monomers either did not have terminal flexible chains, or were endcapped with propargyl groups (again with the acetylene group in the terminal position).^{5,6}

As seen above in Figure 10, the monomers were synthesized by the reaction of the appropriate diol with the appropriate (1-alkynyl) benzoyl chloride. Figure 11 illustrates the benzoyl chloride end group synthesis. As described above, the (1-alkynyl) benzoyl chlorides were synthesized using similar conditions to those of the Heck

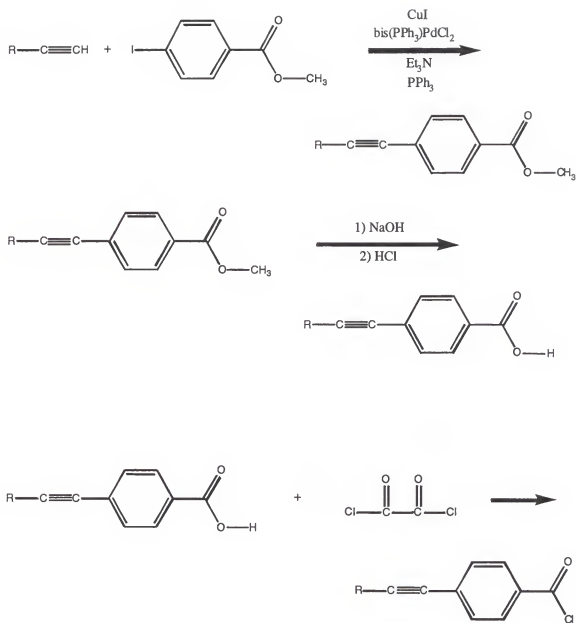


Figure 11. Synthesis of 1-alkynyl benzoyl chloride endgroups.

reaction. This method has been utilized previously for synthesis of (phenylethynyl) benzoyl chlorides and silyl protected acetylene benzoyl compounds.^{56,99-105} In the synthesis of endgroups with flexible chains of <7 carbons, the Heck reaction conditions were modified to avoid polymerization of the less sterically hindered alkynes. For nonyne and decyne, the slurries were heated to 80°C and stirred for 16 to 48 hours to allow for complete reaction. Thus, with careful control of the reaction conditions during the Heck reaction, this method allows the formation of a large variety of internal acetylene containing endgroups.

By refluxing in sodium hydroxide, followed by acidification with HCl, the methyl-4-(1-alkynyl) benzoates were then deprotected to yield their respective 4-(1-alkynyl) benzoic acid. Conversion of 4-(1-alkynyl) benzoic acid to 4-(1-alkynyl) benzoyl chloride was accomplished by refluxing the 4-(1-alkynyl)benzoic acid with oxalyl chloride in benzene. Final monomer synthesis was accomplished through a condensation reaction between two 4-(1-alkynyl) benzoyl chlorides and an aromatic diol. Upon recrystallization, the monomer synthesis was confirmed with elemental analysis and NMR (^1H and ^{13}C).

The nBP series of monomers are relatively insoluble in acetone, small alcohols, and water, but soluble in chloroform (except for the 8BP, which is only slightly soluble in chloroform). The nHQ series of monomers are also insoluble in small alcohols and water, but more soluble in acetone and chloroform than the nBP series (except for the 3HQ, which also has low solubility in chloroform).

Monomer Characterization

The liquid crystalline transition temperatures were determined for the two homologous series of monomers from DSC data. An example is shown in Figure 12 for

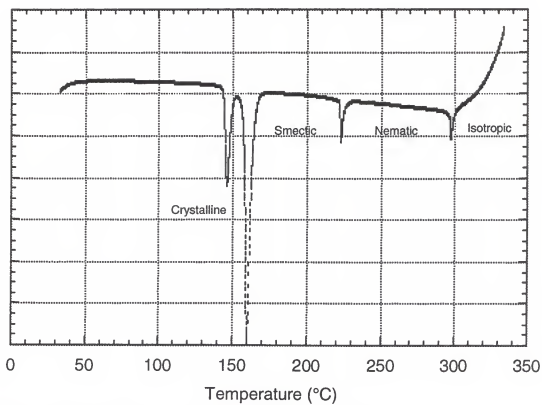


Figure 12. DSC of 6BP. Run at 10°C/min in a nitrogen gas flow.

6BP. All transition temperatures determined from DSC data were confirmed with a hot-stage and cross-polarized optical microscopy. Mesophase identification was accomplished from the optical texture of the monomers during the POM experiments. Transition temperature data for the nHQ and nBP series are presented in Table 1 and Figure 13, Table 2 and Figure 14 respectively. Several studies have been conducted for similar homologous series of small molecule liquid crystals.^{3,7,8,14,106,107} Dewar et al. studied liquid crystals with a molecular architecture similar to that of the nHQ monomer series (for their molecular architecture the acetylene group is replaced with alkoxy groups). In their studies they found only nematic phases for molecules with carbon chains of lengths 1-10, while Arora et al.,⁷ and later Schroeder,¹⁴ found that smectic phases did appear for the same series with alkoxy chains of length >7. As Arora states, the longer hydrocarbon chains play an increasingly significant role in the formation of smectic phases by direct interactions. In other words, the interactions between the alkyl chains become great enough to alter the intermolecular interactions. Thus, the molecules line up such that the alkyl chains interact with each other and the rigid rods interact with each other, leading to a layered structure. This allows greater chain-chain and rod-rod interactions. In the case of the nHQ monomer series, all of the monomers of chain length <8 exhibited only nematic and isotropic phases upon melting, while the monomer with n=8 showed a short lived smectic phase. While these monomers display similar trends for liquid crystalline phases as the *p*-phenylene esters of *para*-benzoic acids, the melting points and the phase transition temperatures are lower for the LCTs. This surprising difference arises due to the substitution of the flexible alkoxy

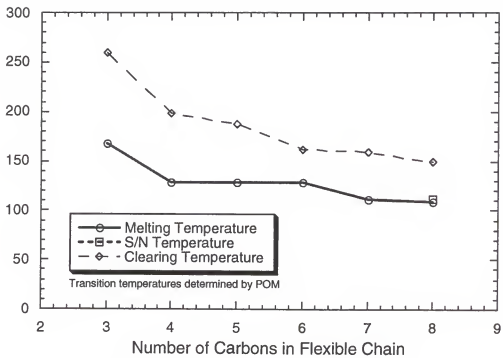


Figure 13. Plot of liquid crystalline transition temperatures for the nHQ series.

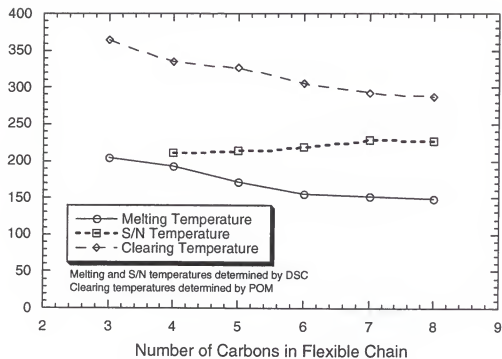


Figure 14. Plot of the liquid crystalline transition temperatures for the nBP series.

Table 1. nHQ series transition temperatures.

Transition temperature from solid or preceding liquid crystal state to:

Number of Carbons, n	Smectic (°C)	Nematic (°C)	Isotropic (°C)
3	N/A	168.00	259.50
4	N/A	129.00	198.10
5	N/A	128.70	187.20
6	N/A	129.30	161.60
7	N/A	111.80	159.60
8	109.00	112.00	150.00

Table 2. nBP series transition temperatures.

Transition temperature from solid or preceding liquid crystal state to:

Number of Carbons, n	Smectic (°C)	Nematic (°C)	Isotropic (°C)
3	N/A	204.00	365.00
4	192.90	211.20	335.00
5	172.00	213.90	326.70
6	154.60	218.70	306.10
7	151.50	228.20	292.20
8	149.00	226.30	286.90

oxygen with the more rigid acetylene group. At first glance, the increase in mesogenic unit size of the LCT monomers should increase the liquid crystalline phase stability, however, the greater polarity of the alkoxy oxygen must contribute more to the intermolecular interactions. Also the acetylene groups may actually be more detrimental to liquid crystalline phase stability because, as mentioned in Chapter 1, liquid crystalline phases are stabilized by mesogens with a constant cross-sectional area and destabilized by either substituents or narrow areas.

As seen in Chapter 1, the homologous series of Schroeder, displays an odd-even effect for the isotropization temperature. In his series, the molecules with an odd number of carbons in the flexible chain lie on a curve above the molecules with an even number. As seen in Figure 13 and Figure 14, the monomers of this study also show an odd-even effect in the clearing temperature. The trends for the isotropization temperatures in both monomer series seem to be converging at $n=8$. This is at a significantly shorter chain length than those of Schroeder's series. Also, unlike Schroeder's series, in the LCT series the curve for the flexible chains with an odd number of carbons is higher than the even number one. This difference is most likely due to the oxygen of the alkoxy chains acting as a flexible carbon.

As seen in Figure 14, the monomers of the nBP series display both a smectic and a nematic phase, except for 3BP that only has a nematic phase. Again, this is due to preferred intermolecular interactions. In this case, once the alkyl chains become long enough, the longer mesogens interact exclusively with other mesogens, thus causing the molecules to line up in layers. Similar to the nHQ series, all of the nBP monomers have isotropic phases. While the melting temperatures for the nBP series are about 40 to 70°C

higher than those of the nHQ series, the isotropization temperatures are 140°C higher. In previous studies of bisacetylene⁶ and bispropargyl⁵ monomers, replacement of the hydroquinone with biphenyl mesogenic unit led to either no effect (bisacetylene monomers did not melt before curing for either mesogen) or increased the melting point by 20°C for the bispropargyl monomers and did not show a clearing temperature before curing for the biphenyl derivative. The higher melting point and higher isotropization temperatures of the nBP series are due to the higher aspect ratio for the monomers, increasing the interactions between the rigid units, consequently increasing the energy necessary to disorder the system. By the same principle, the addition of longer flexible units lowers the stability of the ordered phases. The flexible chains act as a solvent for the mesogenic units, thus interfering in the molecular packing and rigid segment interactions. This leads to both the lower melting points and isotropization temperatures for the monomers with increasing flexible chain length.¹⁷

Conclusions

Two related homologous series of acetylene functionalized liquid crystalline thermoset monomers have been synthesized. These monomers have mesogenic units of aromatic rings either directly linked or linked with ester linkages. The monomers are then endcapped with acetylene groups and terminal alkyl chains. The alkyl chain length varied from 3 to 8 carbons.

The endcapping groups were synthesized by modifying the conditions of the Heck reaction to 4-(1-alkynyl) methylbenzoates. These can then be deprotected and converted to the acid chloride derivative. Through the condensation reaction of the *p*-(1-alkynyl)-benzoyl chloride with a para-functionalized aromatic diols, the liquid crystalline

monomers can be synthesized. It was found that these monomers are hydrophobic, insoluble in small alcohols, but soluble in chloroform (and some in acetone).

The experimental results of the thermal characterization of these monomers show different liquid crystalline phase behavior for the two series. Upon melting, the monomers of the nHQ series only exhibit nematic phases before isotropization, except for 8HQ that has a very small smectic phase. The monomers of the nBP series, however, show smectic and nematic phases for all of the monomers, except for 3BP, which only exhibits a nematic phase before clearing. Due to a higher aspect ratio, the melting points and clearing temperatures for the nBP series were significantly higher than those of the nHQ series were. Also, comparison of the nHQ series with *p*-phenylene esters of *para*-benzoic acids, a homologous non-reactive small molecule liquid crystal series with similar molecular architecture, showed a decrease in melting point and liquid crystalline phase stability. This is attributed to the disruption of the acetylene groups in the cross-sectional area of the mesogenic unit and the loss of the higher polarity of the oxygen in the alkoxy group. Similar to the *p*-phenylene esters of *para*-benzoic acids, the experimental results also showed that within a series, increasing flexible chain length leads to a decrease in the melting point and isotropization temperature, but a stabilization of the smectic phase with respect to the nematic phase.

CHAPTER 3

ISOTHERMAL CURING OF ACETYLENE FUNCTIONALIZED LIQUID CRYSTALLINE THERMOSET MONOMERS

Introduction

As stated in Chapter 2, polymeric matrix materials for composites have continued to increase in usage over the past half a century. Aviation, space exploration, shipbuilding, automotive manufacturing and machine building are all demanding polymer matrix composites with high thermal and chemical stability. Liquid crystalline polymeric matrix materials are emerging as engineering resins due to their unique molecular arrangement. With the increase in use of liquid crystalline thermoset materials, a better understanding of how molecular architecture effects structure during curing is needed.

While there have been a variety of diagrams constructed to illustrate changes a material undergoes during isothermal curing, they are too limited for practical processing use. Traditional transformation diagrams for non-liquid crystalline materials are limited in the information they are able to display. These diagrams offer information about physical transformations during curing, but are not equipped to convey the morphological information needed for liquid crystalline materials. Other experimentally derived transition diagrams for liquid crystalline materials lack the physical information needed during isothermal processing, like gelation. This chapter will describe the synthesis of new liquid crystalline phase-time-temperature-physical transformation diagrams (LCPTTT), and use these diagrams to help elucidate the effects seen from molecular

architecture on the liquid crystalline phase transitions and physical transformations during isothermal curing.

The synthesis and characterization of the two series of acetylene functionalized monomers used in this study is presented in Chapter 2. These monomers are similar to ones reported previously by Douglas et al.⁶ However, unlike the biphenyl and hydroquinone monomers of the bisacetylenes, the monomers presented here do melt and display liquid crystalline phases. The thermal polymerization of these monomers is believed to proceed by a free-radical addition reaction between ethynyl units to generate a polyene network, as seen in Figure 15.^{58,64,108} Trimerization to benzenoid rings is expected to be minimal due to the bulkiness of the flexible chains and the mesogenic unit.

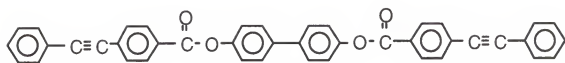
Experimental Section

Materials

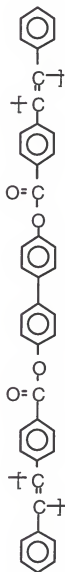
All monomers were synthesized and purified for this study following the procedures in Chapter 2.

Cross-Polarized Optical Microscopy (POM) of Isothermal Cures

POM experiments were conducted using a Nikon Fluorophot microscope (equipped with a video camera and recorder) and a Linkham Scientific Instruments HFS91 hot stage controlled by a TMS 91 temperature controller. Small amounts of the monomers were placed between two 12 mm round, glass microscope cover slips and observed between crossed polarizers. The sample was heated at a rate of 130°C/minute to the desired temperature and then held. The curing was recorded and allowed to continue until twice the time determined for the gelation time of the sample by parallel



Compound 4



Thermoset

Figure 15. Polymerization scheme of acetylene functionalized monomers to thermoset polymer.^{56,58,64,108}

plate rheology. The liquid crystalline transition times and phases were determined by optical texture.

Gelation Determination via Parallel Plate Rheology

Gelation times were determined using a Paar Physica UDS 200, TC 10 Temperature Controller, and modified TEK 600 with parallel plate geometry. The sample chamber and 304-steel plates (a 25 mm diameter top plate and 50 mm diameter bottom plate) were preheated to the desired temperature for 60 minutes in a nitrogen atmosphere. A sample of approximately 0.15 g of monomer was loaded onto the lower plate. The upper plate was then lowered to form a gap of 0.25 mm. The sample was then tested with a 4% oscillating strain of 1hz frequency. The sample's gelation time was determined from the crossover point of the storage and loss moduli ($\tan \delta = 1$).

Results and Discussion

Effect of Molecular Architecture on Liquid Crystallinity

In order to observe the effects of molecular architecture on the liquid crystalline phases seen during isothermal curing, small samples of 3HQ, 3BP, 4BP, and 5BP were isothermally cured on a hot-stage equipped, cross-polarized optical microscope. The samples were observed for twice the time to gelation (as will be discussed in the following section) for the cure temperature. The 3HQ monomer was cured at 230°, 240°, 250°, and 270°C, while 3BP, 4BP, and 5BP were cured at 250°, 270°, 290°, and 310°C. Figure 16, Figure 17, Figure 18, and Figure 19 are examples of the new liquid crystalline phase-time-temperature-physical transformation diagrams (LCPTTT), for 3HQ, 3BP, 4BP, and 5BP respectively, created to illustrate both physical and liquid crystalline transformations which occur during isothermal curing of these materials. The thick black

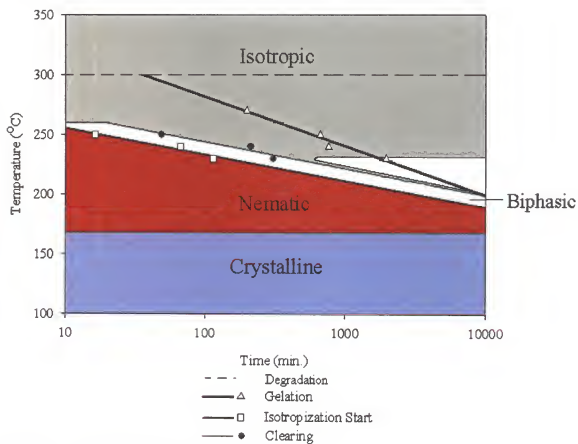


Figure 16. LCPTTT diagram of 3HQ.

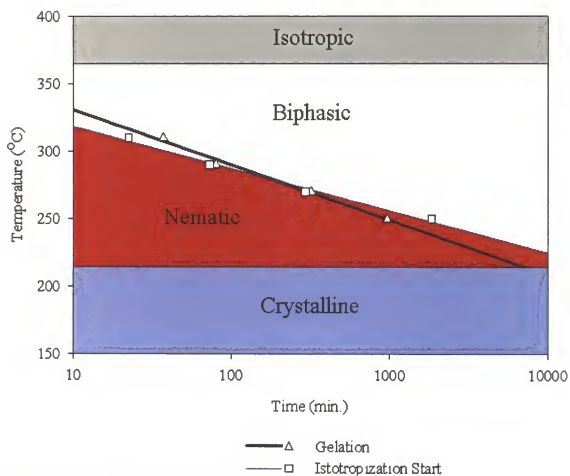


Figure 17. LCPTTT diagram of 3BP.

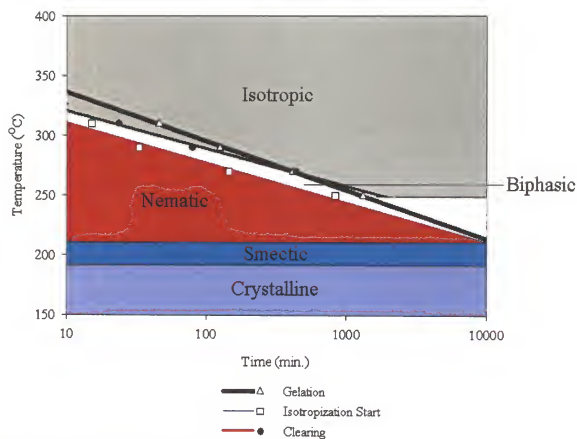


Figure 18. LCPTTT diagram of 4BP.

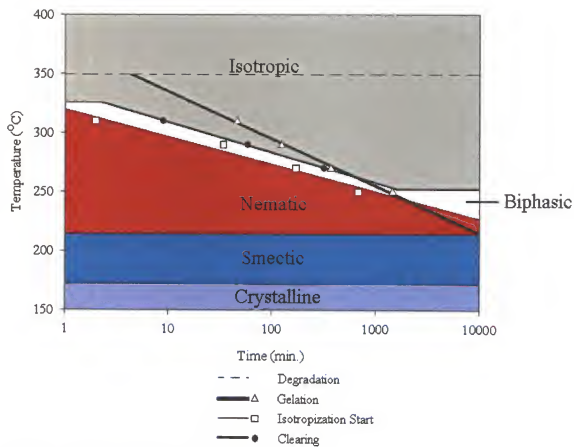


Figure 19. LCPTTT diagram of 5BP.

line represents the time at which the material converts from a liquid to a gel for the isothermal cure temperature. The gel times have been fitted with exponential curves since the time to gelation is controlled by the reaction rate and should follow an Arrhenius relationship with the cure temperature. The liquid crystalline phases are labeled and shaded. The melting, smectic to nematic transformation, and the clearing temperatures of the monomer are also illustrated on the diagrams. The liquid crystalline phase transition times (for the isotropization start times and final clearing times) have exponential curves similar to those for events following an Arrhenius relationship. There are four temperatures tested on each diagram. These points are fitted with exponential curves and extrapolated to the X-axis. The high temperature end is below the degradation temperature of the monomer, while the low temperature end is above the smectic and crystallization transition temperatures for the monomers. Since the area in which these curves are plotted should not have any additional confounding factors, the extrapolations should be valid.

As can be seen in all four of the diagrams, at the temperatures tested, these materials transform from an ordered nematic liquid crystal to either a biphasic nematic/isotropic or an isotropic material (except for 3HQ at 270 which starts in the isotropic phase). An example of 5BP isothermally cured at 310°C progressing from the nematic phase to the isotropic phase is demonstrated in Figure 20. The loss of liquid crystalline order is due to the lack of a spacer group between the polymer backbone and the mesogenic units. The polymerization causes the rigid units to come closer towards each other, increasing the steric interactions. During the initial stages of polymerization,

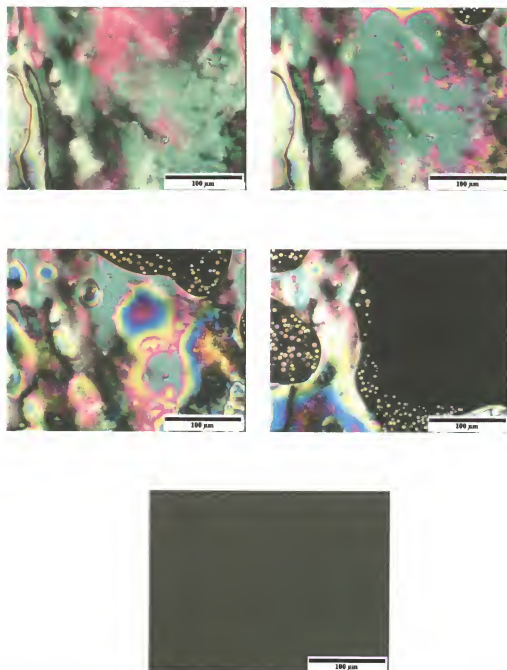


Figure 20. Series of polarized optical micrographs of 5BP progressing from nematic to isotropic while cured isothermally at 310°C. Elapsed time from when monomer reached 310°C is 12 minutes. Scale bar = 100 μm.

while the viscosity is low, the rods splay away from each other, increasing the degrees of freedom, and disrupt the molecular ordering. Typically for side-chain LCs, a flexible spacer group between the mesogenic unit and the backbone decouples the mesogen from the backbone and allows more degrees of freedom while still maintaining the molecular ordering.

The retention of a biphasic structure (seen for all testing temperatures of 3BP and the lowest temperature for 4BP) is partially due to vitrification of the material, or ending of the testing period, before complete isotropization. The retention of a biphasic region for 5BP tested at 250°C is different. In this case, toward the end of the transformation from nematic to isotropic, the material begins to reorder. It begins as pinpoint birefringent spots that grow and merge as curing continues. As seen in the LCPTTT diagram of Figure 16, for 3HQ at 230°C, the material completely converts to an isotropic phase, but regains some molecular ordering before vitrification. This is shown in the micrographs of Figure 21. As the network grows, the reemergence of an ordered phase may be because of an increase in concentration of rigid rods per unit volume at higher conversions. This is similar to the reemergence, or initial emergence, of liquid crystalline phases seen for specific bisacetylenes,⁶ bisnadimides,⁴⁸ and liquid crystalline epoxies.^{37,53} In those studies, the formation of liquid crystalline phases was attributed to an increase in axial ratio from chain extension. However, for the nBP and nHQ series the reordering often occurs after the three-dimensional network is already forming. This is indicated since the material initially begins to convert to an isotropic phase during initial chain extension. The initial loss of liquid crystalline order may be reduced or even prevented if the mesogen was decoupled from the functional groups. This may allow a

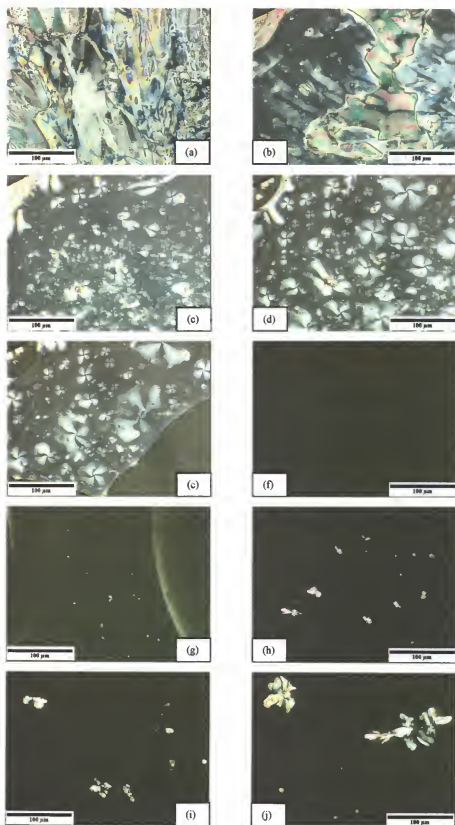


Figure 21. Series of optical micrographs of 3HQ as it is cured isothermally at 230°C. Micrographs are taken at approximately (a) 1, (b) 70, (c) 80, (d) 170, (e) 200, (f) 530, (g) 880, (h) 1630, (i) 1700, (j) 1980 minutes after reaching 230°C. Scale bar = 100 µm.

greater amount of molecular order in the final material since the reemerging ordered phases occur when the material is of a higher viscosity. The higher viscosity prevents complete molecular order for the material. The phenomena of a reemerging ordered phase might also exist in the 3BP and 4BP monomers but is hidden by the already existing ordered phase. The retention or reformation of an ordered phase is only seen when the material is cured at lower temperatures due to a decrease in the clearing temperature, compared to that of the uncured monomer. Increasing the flexible chain length requires lower curing temperatures for formation of a cured product with molecular order. This is due to a destabilization of liquid crystalline phases by the longer chains, thus lowering the clearing temperature.

Effect of Molecular Architecture on Gelation Times

The gelation times for the isothermal curing at 270°C for the twelve monomers were determined using parallel plate rheology. The ~0.15g samples were tested with a 1hz oscillating strain of 4%. The criteria for gelation was the crossover point between the G' and G'' curves. This is determined from when $\tan \delta$, also known as the damping and is defined as G''/G' , is equal to 1. Gel times were recorded as the last data point in which $\tan \delta$, factor was ≥ 1 . An example of the evolution of G' , G'' , and damping factor is shown in Figure 22. Figure 23 and Figure 24 present the gel times for the nHQ and nBP series, respectively. The error bars for these plots (except for 4BP and 8BP) are the standard deviation from 6 runs of 3BP at 270°C. For 4BP and 8BP, the error bars are the standard deviation from 4 runs of those monomers at 270°C.

In previous studies of thermosetting systems^{75,77,84,86,90,91,95,96}, it was determined that chemical conversion at the gel point is constant for a given reactive

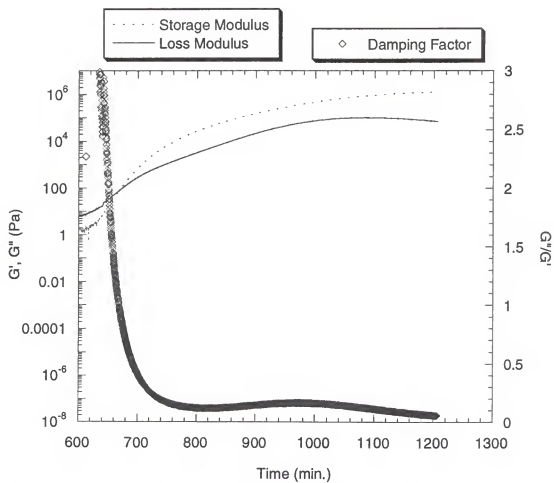


Figure 22. Rheological data for 3HQ while cured isothermally at 250°C.

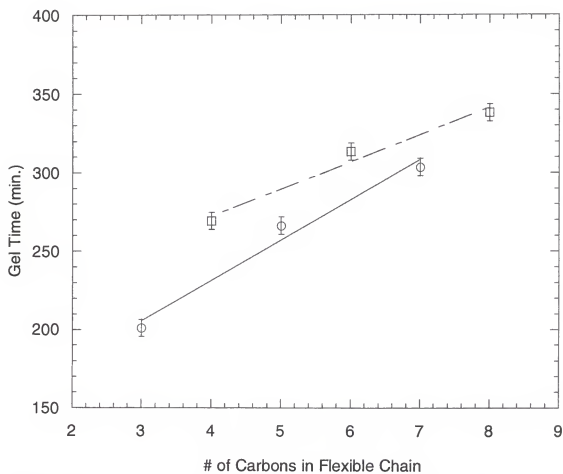


Figure 23. Plot of gel times for the nHQ series tested at 270°C, 1 hz, and 4% strain.

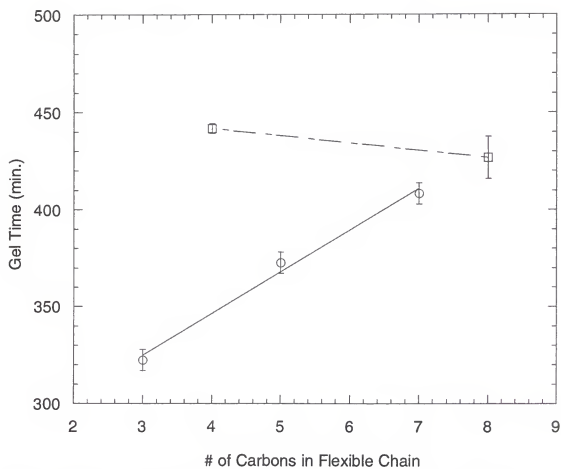


Figure 24. Plot of gel times for the nBP series tested at 270°C, 1 hz, and 4% strain.

thermosetting system, independent of the time-temperature path taken. Initially it would be thought that as the flexible chain length linearly increases, the gel time would also linearly increase due to a rise in steric hindrances. As seen in Figure 23 and Figure 24, there is an increase in the time to gelation with increasing chain length, however, the increase is not linear. The data point for 6BP has been excluded. When tested multiple times, the time to gelation for 6BP ranged from 220 minutes to 480 minutes, yielding a value around 326 minutes with a standard deviation of about 111 minutes. The other monomers had a much smaller variability in their values with standard deviations ranging from 2 to 10 minutes.

An odd-even effect is seen for the gel times of both series. This is especially surprising for the nHQ series due to the fact that the monomers are isotropic at this temperature, as seen in Table 1. The lack of local order discounts the traditional reasoning of end-group interactions being responsible for the occurrence of an odd-even effect.¹⁵

Comparison of the gel times for monomers with equal length but different central mesogenic units, 3HQ and 3BP for example, shows that the monomers with the shorter mesogen gel quicker. This may be due to an increase in molecular mobility available to the smaller, more flexible monomer or a higher reactivity of its acetylene groups. The effect from the resident time a monomer spends in a phase during curing is also of interest. From Table 2, at 270°C, the nBP monomers are in the nematic phase. However, as mentioned in the previous section, the monomers of the nBP series undergo a transformation from nematic liquid crystals to isotropic liquids during the isothermal cures. Due to the differences in both curing rates and liquid crystalline phase stabilities

for the monomers in this series, some are gelling as nematic liquids while others are gelling in the isotropic phase. This greatly complicated the cure kinetics and the times to gelation. Several previous studies of free radical polymerization in liquid crystalline phases versus isotropic phases have shown an enhancement in the polymerization rate for polymerization in a liquid crystalline phase.^{6,109,110} This possible rate enhancement complicates the relative gelation times within the series since the monomers are curing in nematic phases for different amounts of time. To determine whether or not the cure rates are significantly influenced only by temperature or also by other influences, Arrhenius plots for the gelation of monomers 3HQ, 3BP, 4BP, and 5BP are presented in Figure 25, Figure 26, Figure 27, and Figure 28, respectively. The Arrhenius plots are all linear. This indicates that there does not appear to be any affect on the reaction rates due to the amount of time a monomer spends in the nematic phase, only on the temperature at which it is being cured. While the reaction mechanism for these monomers has not yet been elucidated, the activation energies calculated from the Arrhenius plots for 3BP, 4BP, and 5BP are all around 143.5 kJ suggesting similar mechanisms. The activation energy for the 3HQ monomer is 122 kJ, indicating a lower energy barrier for the polymerization than that for the nBP monomers. This may be due to the greater molecular mobility of the smaller monomer, thus requiring less energy.

As seen in Figure 24, the gel times of the nBP series also show a possible odd-even effect; however, the even curve shows very little change with increasing chain length. When compared to the shape of the curves for the nHQ series, this lack of increase in gel times with increasing chain length implies independence for the cure rate with respect to the chain length for chains of even carbon length. Also of note is that, for

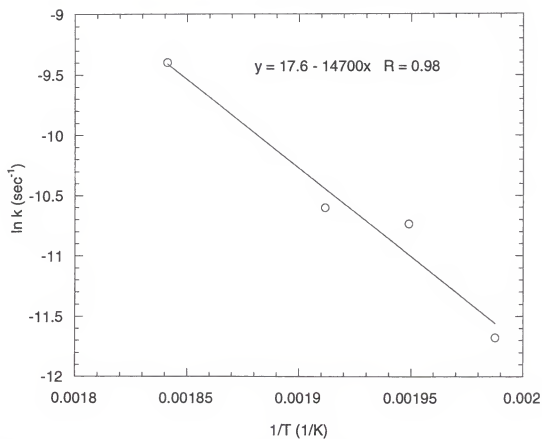


Figure 25. Arrhenius plot for the gelation of 3HQ. Activation energy calculated to be 122 kJ.

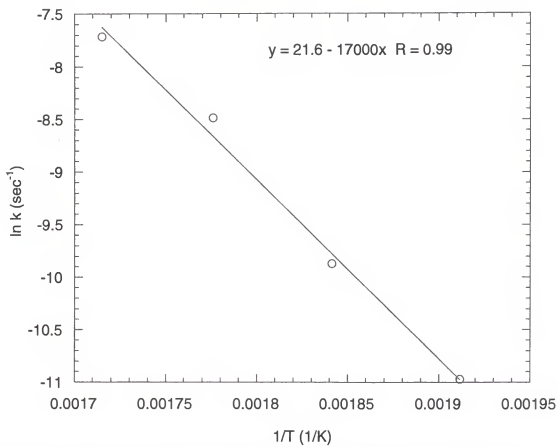


Figure 26. Arrhenius plot for the gelation of 3BP. Activation energy calculated to be 142 kJ.

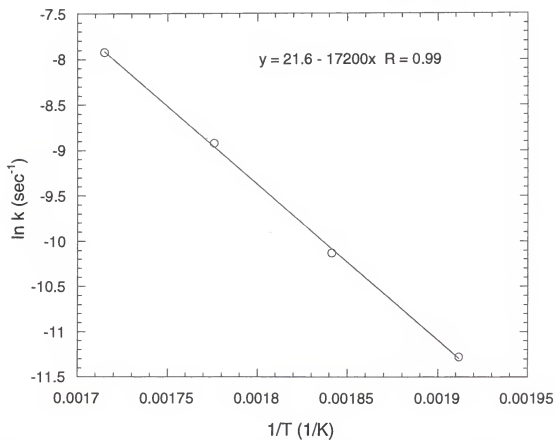


Figure 27. Arrhenius plot for the gelation of 4bp. Activation energy calculated to be 143 kJ.

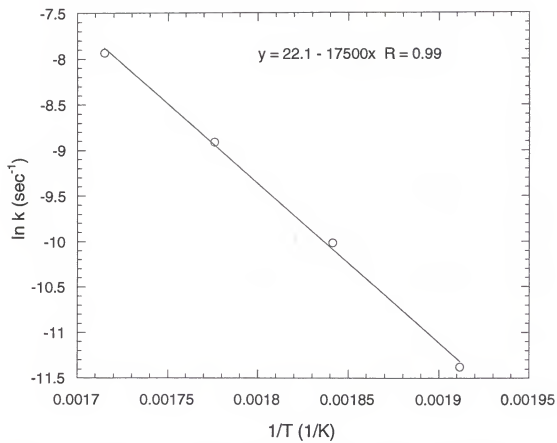


Figure 28. Arrhenius plot for the gelation of 5BP. Activation energy calculated to be 145 kJ.

both series, the odd and even curves for the gel times seem to be converging at around $n=8$. This is similar to the trend seen for the clearing temperatures of the monomers. The convergence implies that the differences in cure kinetics between chains of odd and even length decrease with increasing chain length, and might even disappear with chains of a critical length.

Conclusions

The effects of molecular architecture on the liquid crystalline phases and times to gelation for two series of acetylene functionalized LCT monomers were studied. The monomers could be cured at temperatures between 230°C and 310°C. Through the use of a rheometer with parallel plate geometry, a hot-stage, and a cross-polarized optical microscope the new liquid crystalline phase-time-temperature-physical transformation diagrams (LCPTTT) were constructed for four of the monomers synthesized in Chapter 2. These diagrams illustrate that the monomers change from nematic liquids to isotropic or biphasic gels during isothermal curing. However, reemergence of an ordered phase occurred if the monomers were cured at low enough temperature. The critical temperature for ordered phase retention in the final vitrified material is inversely proportional to the length of the flexible chain. This may be due to a destabilization of the liquid crystalline phases with increasing chain length. Also, as expected from the characterization of the monomers, the nBP series had greater liquid crystalline phase stability during isothermal curing than the nHQ series. The liquid crystalline phase transitions, the onset and completion of isotropization, did seem to follow an Arrhenius relationship with temperature. It had previously been established that gelation occurs at a specific extent of conversion for a monomer, regardless of the time-temperature path

taken to gelation for the thermosetting system. However for the nHQ and nBP monomers, the curves for gelation and the liquid crystalline transitions had different slopes. This may indicate that the liquid crystalline transitions are controlled not only by extent of monomer conversion, but by a combination of conversion and temperature.

The gel times for the two series of monomers were compared for isothermal cures of 270°C. It was shown that monomers of the nHQ series gelled quicker than the monomers of the nBP series with the same flexible chain length. This is attributed to a decrease in molecular mobility with increasing mesogenic unit length. Both series did show an increase in gel times with increasing chain length, however, the increase was not in a linear manner as expected. Instead, an odd-even effect was seen in both series. Since the nHQ series was cured in the isotropic phase at 270°C the presence of an odd-even effect is especially surprising since traditional reasoning for this effects requires the molecules to be in an ordered state. Also surprising was the fact that the even curve for the nBP series was not increasing with increasing chain length. This shows an enhancement or leveling of the cure rate with increasing chain length, at least for chains of even length. The gel times for the nBP series may be complicated by the fact that the monomers spend different amounts of time in liquid crystalline phases. It is thought that this may be attributed to monomers that retain their nematic ordering to have an enhancement in the cure kinetics. However, Arrhenius plots of 3BP, 4BP, and 5BP all show linear slopes even though they have different residence time in nematic phases, depending on the temperature. The activation energies for the nBP monomers were calculated to be essentially the same, yet significantly greater than that of 3HQ. Both series also appeared to be converging at around $n=8$, thus indicating the loss of the odd-

even effect for monomers with chains of greater length. This is similar to the convergence seen for the clearing temperatures of the monomers.

CHAPTER 4

HIGH TEMPERATURE STABILITY OF A NOVEL PHENYLETHYNYL LIQUID CRYSTALLINE THERMOSET

Introduction

Polymer matrix composites are increasingly replacing other conventional materials in engineering applications requiring high strength to weight ratios, high temperatures, and good chemical resistance. Liquid crystalline polymeric matrix materials are emerging as engineering resins due to their unique molecular arrangement. The liquid crystalline order found in these materials arises from rigid chain segments connected to other flexible segments.^{97,98}

As mentioned in Chapter 1, since these polymers are finding use as matrix materials in composites for the aerospace industry, there are special physical properties required of them. One of the critical requirements is that the material retains useful properties at 400°C and higher.⁷⁴

The most common method for comparison of high temperature stability of experimental materials is through dynamic thermogravimetric analysis (TGA). By measuring the weight remaining during constant heating rates, TGA data indicates the threshold temperature for the degradation of a polymer network. Comparison of these threshold temperatures (for the same heating rate) yields a relative stability of polymer structures.⁷⁴

Isothermal thermogravimetric analysis (IGA) yields data for long term polymer stability at a predetermined temperature. This allows the determination of a material's use for extended periods of time at high temperatures.⁷⁴

While the monomers discussed in Chapters 2 and 3 have been designed for high temperature applications, they were mostly designed to yield information about the affects of molecular architecture on liquid crystallinity and physical phases. This chapter will discuss a closely related fully aromatic monomer, which was specifically designed for extremely high temperature applications. Comparison to the flexible monomers and examination of its thermal stability will be discussed.

Experimental Section

Materials

All chemicals were used as received. Methyl-4-iodobenzoate, bis-(triphenylphosphine)- palladium(II)chloride, triphenylphosphine, copper(I)iodide (98%), triethylamine, oxalyl chloride, sodium hydroxide, concentrated hydrochloric acid, diethylether, dimethylformamide, methanol, benzene, and biphenol (97%) were all received from Acros. The phenylacetylene (98%) was received from Aldrich.

Synthesis

The synthesis of the fully aromatic phenynylethynyl functionalized biphenol derived monomer (PEBP) is shown below in Figure 29.

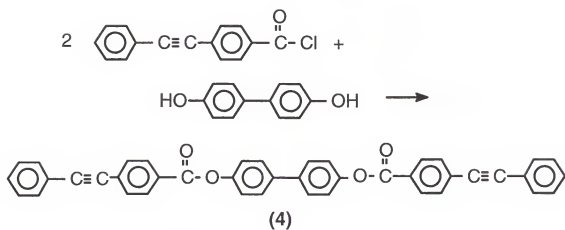
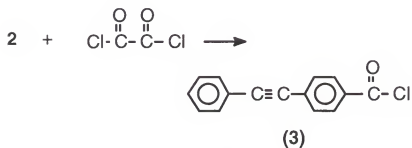
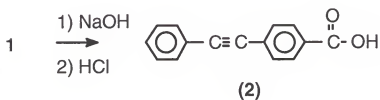
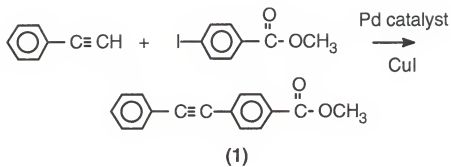


Figure 29. Synthesis of PEBP monomer.⁵⁶

Methyl-4-(phenylethynyl)benzoate (1)

A 500 mL 3-neck flask with stir-bar was heat/vacuum dried and flushed with nitrogen. Methyl-4-iodobenzoate (12.8943 g, 0.049 mol), phenylacetylene (8.1 mL, 7.533 g, 0.074 mol), triethyl amine (150 mL, 108.9 g, 1.076 mol), triphenyl phosphine (0.0986 g, 0.38 mmol), bis(triphenyl phosphine)palladium (II) chloride (0.0471 g, 0.07 mmol), and copper iodide (0.0220 g, 0.12 mmol) were then added. The light yellow slurry was stirred under nitrogen for 7 hours at 80°C. The solution was cooled to room temperature overnight. The solution was then filtered, and the solid was washed with diethyl ether until white in color. The yellow filtrate was then reduced under vacuum to yield a light orange solid that was dried at room temperature under vacuum overnight. Hexanes (250 mL) was added and the slurry was stirred vigorously for two hours. The solid was allowed to settle from the solution for 6 hours, and was then cannula filtered. The resulting light orange solid was dried overnight in vacuum yielding 8 g of light orange solid, compound **1** (70%). EA: Theory: 81.37% C, 5.08% H, 13.55% O; Actual: 81.95% C, 4.97% H, 13.08% O. 300 MHz ¹H-NMR (DMF-d7): δ = 3.9 (s, 3 H, CH₃), 7.4 (t, 2 H, aromatic), 7.6 (m, 2 H, aromatic), 7.7 (m, 2H, aromatic), 8.1 (t, 2H, aromatic). 75 MHz ¹³C-NMR (DMF-d7): δ = 52.6 (-CH₃), 89.2 (acetylene), 92.9 (acetylene), 123.0, 128.3, 129.5, 129.9, 130.2, 132.4 (aromatic), 166.5 (-COO-).

4-(phenylethynyl) Benzoic Acid (2)

Sodium hydroxide (1.6580 g, 0.0415 mol), water (22.4 mL), and methanol (22.4 mL) were combined and stirred until the sodium hydroxide was dissolved completely. While stirring, compound **1** (7.7333 g, 0.0327 mol) was added to the solution. The orange/beige slurry was then heated to reflux. An additional 4.75 g of sodium hydroxide,

25 mL of water, and 25 mL of methanol were added to the slurry and heated to reflux for 3 hours. The highly basic slurry was then allowed to cool to room temperature. Dimethylformamide (700 mL) was then added to the slurry, and heated to a gentle boil. The solid dissolved leaving a very dark orange solution, which was acidified with concentrated HCl. The resulting suspension was allowed to cool to room temperature and then was diluted with water (while maintaining a highly acidic pH) to help precipitate all solid from the DMF solution. Finally, the solid was filtered from the slurry and dried in a vacuum oven at 80°C for 24 hours to yield 6.819 g (93.7%) of compound **2**. Due to the low solubility of compound **2**, NMR spectra could not be obtained. EA: Theory: 81.1% C, 4.5% H, 14.4% O; Actual: 80.8% C, 4.57% H, 14.61% O.

4-(phenylethynyl) Benzoylchloride (3)

Compound **2** (6.8190 g, 0.0307 mol) was placed in a nitrogen-flushed 500 mL, 3-neck round bottom flask containing 43 mL of benzene. Oxalyl chloride (7 mL, 9.7355 g, 0.0767 mol) was slowly added via syringe. The light beige suspension was stirred and heated to reflux for 3.5 hours, during which the color gradually changed to crimson. The solution was then allowed to cool to room temperature overnight. All volatiles were then removed via vacuum. The resulting solid was dried in vacuum at 35°C overnight to yield 6.8427 g (86.9%) of compound **3**. Due to the moisture sensitivity of compound **3**, monomer synthesis was accomplished as soon as possible after synthesis of **3**. Note: use extreme caution when handling oxalyl chloride, and only handle in a ventilated hood.

PEBP (4)

Biphenol (0.9958 g, 5 mmol), diethyl ether (14 mL), and triethyl amine (1.8 mL, 0.0133 mol) were put in a 3-neck round bottom flask and stirred in an ice water bath for

0.5 hours. Compound **3** (3.4221 g, 0.0133 mol) was slowly added. The thick slurry was diluted with 5 ml of diethyl ether, and then was stirred at room temperature for 3.5 hours. At this point, ether and any remaining amine were removed via vacuum. Warm water (50 ml) was then added and stirred overnight with the beige hydrophobic solid. The solid was then filtered and recrystallized once in a DMF/acetonitrile (70/60 v/v) solution at 110°C. The resulting crystals were then washed with acetonitrile and were then recrystallized from 150 mL of boiling DMF. The white crystals were then filtered and dried in a vacuum at 80°C overnight to yield 2.4662 g (82.97%) of PEBP. Due to the low solubility of PEBP, NMR spectra could not be obtained. EA: Theory: 84.86% C, 4.37% H, 10.77% O; Actual: 84.69% C, 4.54% H, 10.77% O.

Room temperature solubilities of compounds **2** and **4** were found to be very low in acetone, toluene, hexanes, DMF, acetonitrile, DMSO, water, benzene, and methanol.

Curing of PEBP

PEBP (~2 g) was loaded into an alumina boat lined with aluminum foil. The boat was then placed in a tube furnace under a flowing nitrogen atmosphere. The furnace was heated to 350°C at a rate of 10°C/min. The monomer was allowed to cure at 350°C for two hours and then cooled to room temperature. The resulting glassy solid was opaque and brownish-orange.

Polarized Optical Microscopy (POM)

POM experiments were conducted using a Nikon Fluorophot microscope and a Linkham Scientific Instruments HFS91 hot stage controlled by a TMS 91 temperature controller. Small amounts of PEBP were placed between two 12 mm round, glass microscope cover slips and observed between crossed polarizers. The sample was heated

at a rate of 10°C/minute to 400°C. The clearing temperature and liquid crystalline phase were determined by optical texture.

Wide Angle X-ray Scattering (WAXS)

WAXS was conducted using a Siemens General Area Detector Diffraction System (GADDS[®]) equipped with the Siemens HI-STAR detector. X-rays were generated by a Kristalloflex 760 2.2 kW generator. The sample was mounted about 1 cm from a long, fine focus collimating tube with cross-coupled Göble mirror monochromator with 500 µm collimation. The sample-to-detector distance was 10 cm. An additional 300 µm point collimation was provided by a pinhole mounted in the sample holder situated flush to the sample to reduce edge scattering noise. A 4° beam stop was mounted 40 mm behind the sample. The WAXS data were used to confirm the assignment of the liquid crystalline phase found in the crosslinked resin.

Thermal Analysis

Thermogravimetric analysis (TGA), isothermal thermogravimetric analysis (IGA) and differential scanning calorimetry (DSC) were performed using a Seiko Instruments SSC5200 TG/DTA 320 and SSC5200 DSC220C with an SDM5600H Data Station. The TGA experiments were carried out in streams of nitrogen or air over the temperature range of 25°C to 1000°C. The heating rates used were 3°, 5°, 7°, 10°, 13°, 17°, 20°, 23°, 30°, 40°, and 50°C/minute. Isothermal TGA experiments were also conducted for temperatures of 320°, 330°, 340°, 350°, 360°, 370°, 380°, 390°, 400°, and 410°C in nitrogen and air atmospheres. The melting point and cure exotherm for the uncured monomer were determined from the extrapolated onsets of a DSC experiment in a

nitrogen gas flow with a heating rate of 10°C/minute. The cured material was also tested in the DSC under the same conditions. Comparison of the exotherms of curing for PEBP and the crosslinked resin showed a very high degree of cure for the cured resin.

Results and Discussion

Synthesis of Monomer and Cured Thermoset

Preparation of PEBP is shown in Figure 29. Reaction of methyl-4-iodobenzoate with phenylacetylene in the presence of a palladium catalyst and heating yields the phenylethynyl-substituted methylbenzoate, compound **1**. This compound is converted to the para-substituted benzoic acid, compound **2**, and further converted to the benzoyl acid chloride by reacting compound **2** with oxalyl chloride, to yield compound **3**. Two equivalents of compound **3** are then coupled to biphenol, through a condensation/esterification reaction to yield the bis(phenylethynyl)-functionalized monomer, PEBP.

The monomer was cured by bulk polymerization in the nematic liquid crystalline phase, without the use of catalysts or initiators, under a nitrogen atmosphere. The resulting crosslinked resin is a glassy, insoluble, dark orange, opaque solid. The cured solid is not only a highly crosslinked resin, but also one which retains the nematic liquid crystalline order of the parent monomer. This is very different than the related monomers described in Chapter 2 and Chapter 3 since these monomers typically lost most of their molecular ordering upon curing, especially at higher temperatures.

NMR spectroscopic data were unable to be collected for compounds **2-4** due to low solubility in common solvents. Therefore, confirmation of the synthesis of these compounds has been accomplished from reactivity, solubility, and elemental analysis.

Characterization of Monomer and Thermoset

PEBP is a highly aromatic, low molecular weight, crystalline monomer with very low solubility in common solvents. The crystalline monomer melts into a free flowing nematic liquid crystal. As determined from the DSC data shown in Figure 30, the melting temperature and the temperature for the extrapolated onset of curing are 268°C and 313°C respectively. The fact that the monomer melted before curing was somewhat unexpected, due to results seen from a monomer previously synthesized with a similar molecular structure.⁶ These two monomers only differ by their terminal functional groups. In this study the terminal group is the phenylethynyl group, while in the previous case the endgroup was capped with the ethynyl group. The ethynyl-terminated monomer did not melt before curing at 211°C. The fact that the ethynyl monomer did not melt is understood from the combination of the rigidity of the molecule and the lack of side groups to disrupt the molecular packing.

Since the rigidity of the ethynyl monomer and the phenylethynyl monomer are similar, it is thought that the observance of a melting temperature for this LCT is due to the difference in reactivity between the phenylethynyl group and the ethynyl group. Since the extrapolated onset of curing for the phenylethynyl monomer does not occur until 313°C, ~100°C higher than that of the ethynyl monomer, the phenylethynyl monomer has the opportunity to melt before curing. In contrast, the higher reactivity of the ethynyl group causes the monomer to cure before the crystal can melt. In this context, it is interesting to note that the melting temperature of the phenylethynyl monomer is 268°C, midway between the exotherms of cure for the two monomers. The melting point of PEBP is about 60°C higher than the highest melting nBP or nHQ monomer. This is

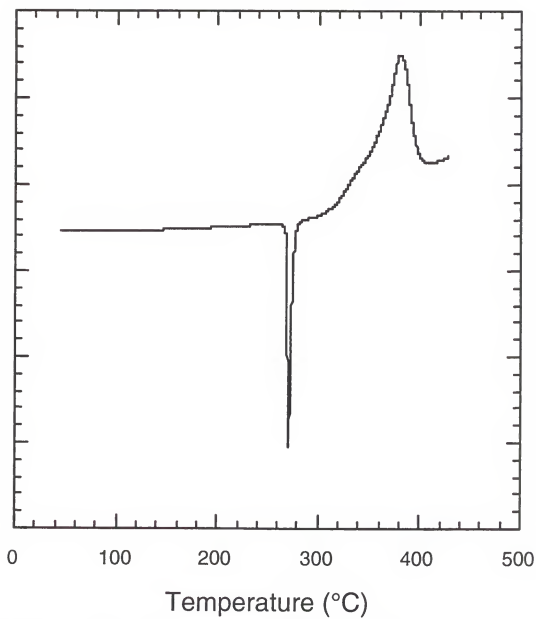


Figure 30. DSC of PEBP. Run at 10°C/min in a nitrogen gas flow.⁵⁶

expected since the flexible chains of the monomers in the nHQ and nBP series disrupt the molecular packing in the crystals, thus lowering the melting points.

The degradation difference between PEBP and the flexible chain monomers is also very significant. The TGA of the PEBP monomer begins to display significant weight loss at temperatures greater than 400°C while the nBP and nHQ monomers lose weight at temperatures around 350°C or less. The difference is attributed to the replacement of the alkyl chains with aromatic rings in PEBP. This will also translate into a cured material with greater thermal stability due to the absence of the aliphatic chains, and possibly a higher degree of cure due to the ability to be cured at significantly higher temperatures.

The temperature difference between the monomer's melting temperature and cure onset temperature provides a processing window of about 45°C for use in melt processing. The melting of the crystals of PEBP were observed using POM. The monomer melted into a liquid crystal with a texture and viscosity consistent with nematic liquid crystals.

Curing the monomer at 350°C for two hours in a nitrogen atmosphere yielded a glassy, opaque, dark orange solid. A DSC experiment was run at 10°C/min from 30°C to 450°C for the crosslinked resin; neither a melting point nor cure exotherm were evident. POM and WAXS experiments confirmed that the LCT had retained the nematic liquid crystalline. The full retention of liquid crystalline ordering was surprising when compared to the data for the flexible monomers in Chapter 3. While the phenyl rings do increase the rigidity of the monomer, their bulkiness was expected to destabilize the liquid crystalline stability, especially at the extremely high curing temperature of 350°C.

Thermal Analysis of the Crosslinked Resin

TGA of PEBP

TGA curves at a heating rate of 10°C/min are shown in Figure 31 for air and nitrogen atmospheres. Table 3 and Table 4 list the TGA data for the crosslinked resin in both nitrogen and air atmospheres with multiple heating rates. As can be seen from these tables, the LCT does not begin to lose weight until >350°C, even in air. The 5% weight loss for the rate of 10°C/min in air and nitrogen occurs at 491°C and 507°C respectively. These temperatures are greater than those for other aromatic polyesters; for example poly(*p*-hydroxybenzoic acid) reaches 5% weight loss in the same conditions by 300°C.⁷⁴ The increase in thermal stability of the LCT can be attributed to the network structure, which prevents complete degradation in the case of the cleavage of a single bond. The network also keeps the severed chains in close proximity, thus allowing recombination of the free radicals.⁷⁴ Other aromatic crosslinking phenylethynyl resins have been examined for their thermal stability in air and inert atmospheres.^{59,62,66,69} This liquid crystalline thermoset has an intermediate thermal stability in air relative to other phenylacetylene derived polymers. For example, the onset for thermal degradation for poly(phenylacetylene)⁷⁴ is 200°C lower than this LCT. This may be due to two possibilities. First, the higher thermal stability may be due to the network structure proposed for this LCT, as stated above. The second possibility may be due to the hindrance of the diffusion of oxygen into the liquid crystalline thermoset, thus preventing oxidation of the network. Previous studies of the gas transport properties of LCPs have shown decreased diffusivities for gasses through polymers with nematic liquid crystalline order.¹¹¹ In non-oxidative atmospheres, the thermal stability of the LCT is

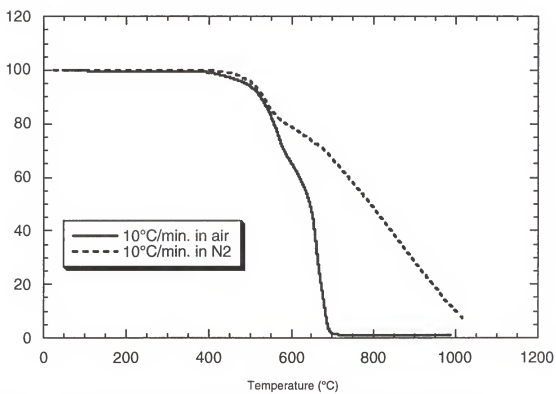


Figure 31. Comparison of isochronal degradation of PEBP in air and nitrogen.

Table 3. Thermal stability data for cured thermoset in nitrogen.⁵⁶

Heating Rate (°C/min)	Temp. for Onset of Weight Loss (°C)	Temp. for 5% Weight Loss (°C)	Temp. for 10% Weight Loss (°C)
3	362	467	502
5	375	474	512
7	404	495	523
10	422	507	533
13	421	510	538
17	425	512	541
20	425	517	543
23	422	511	544
30	424	532	557
40	448	536	558
50	449	534	561

Table 4. Thermal stability data for cured thermoset in air.⁵⁶

Heating Rate (°C/min)	Temp. for Onset of Weight Loss (°C)	Temp. for 5% Weight Loss (°C)	Temp. for 10% Weight Loss (°C)
3	355	461	493
5	386	477	510
7	381	485	518
10	397	491	525
13	397	497	531
17	386	502	539
20	402	512	543
23	407	510	543
30	431	527	554
40	428	532	557
50	439	540	565

20°C to 170°C higher than acetylene- terminated-polysulfone (ATS)⁶⁶ and tri- or tetrakis-(phenylethynyl)benzene.⁶⁹ The increase in thermal stability is due to the combination of the resonance structures of the polyene and the ester linkage, and the rigid character of the LCT. Para- linkages have been found to be more thermally stable than ortho- or meta-, which are present in tri- and tetrakis-(phenylethynyl)benzene.⁷⁴ While ATS has the para- linkage of aromatic rings, the sulfone linkage is more susceptible to degradation than the ester linkages of the LCT.⁶⁶

The method of Nam and Seefris¹¹³ for the determination of activation energies at various percent weight losses in air and nitrogen was utilized to calculate activation energies for the TGA data of PEBP. This was accomplished by making use of the relationship between the heating rate, rate constant, and the conversion functional relationship:

$$d\alpha/dt = q \, d\alpha/dT = k(T) \, f(\alpha)$$

where q is the heating rate, $k(T)$ is the rate constant, and $f(\alpha)$ is the conversion functional relationship. Since there is an Arrhenius type of relationship between the rate to achieve a certain percent conversion and the temperature at which that percent conversion occurs, the heating rate can be related to the conversion temperature through:

$$\text{Log } q = -0.457 \, E_a/RT + \text{const.}$$

Therefore, the log of the heating rates was plotted versus $1/\text{temperature}$ at which a percent conversion occurred. The slope of the line yields the activation energy for that percent conversion. The plots of the activation energies for the various percent conversions in air and nitrogen atmospheres are presented in Figure 32. As can be seen from the plots, the activation energies for the initial percent conversions for air and

nitrogen are the same for both air and nitrogen atmospheres. Therefore, the activation energies for the initial degradation processes are independent of the atmosphere in which they occur.

IGA of PEBP¹¹³

Plots of IGA data for the isothermal weight loss of PEBP at three different temperatures are given in Figure 33. As expected, the higher the temperature, the greater the weight loss for the same length of time. However, as can be seen from the plot, the rate of weight loss is inversely proportional to the extent of conversion. In other words, the greater the extent of degradation, the slower the rate of degradation becomes. Figure 34 plots the IGA curves for PEBP tested at 350°C in both air and nitrogen atmospheres. As expected, the rate of degradation is greater for the air atmosphere than the nitrogen. The lines for the initial few percent of degradation are from polynomial fits of the data. These polynomial lines were used to determine the initial rate of degradation for the isothermal test.

Using the relationship of: $\log R_{t0} = \log A - (E_A/2.3R)(1/T)$, where R_{t0} is the initial rate of degradation, activation energies were determined for both the air and nitrogen atmospheres. The Arrhenius plots for both air and nitrogen atmospheres are presented in Figure 35. As seen on the plot, the activation energies for both air and nitrogen are about the same. This was surprising since it implies that an oxidative process is not an important mechanism in the thermal degradation of this material. For the initial few

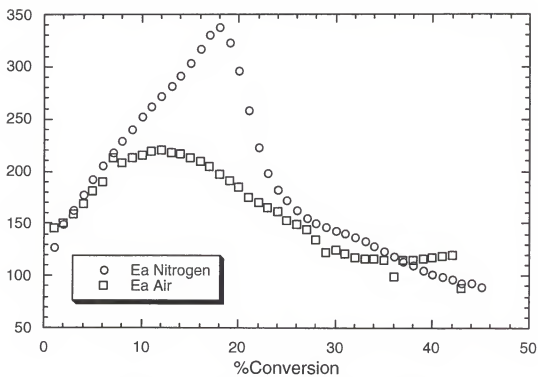


Figure 32. Activation energies from the isochronal TGA data of PEBP.

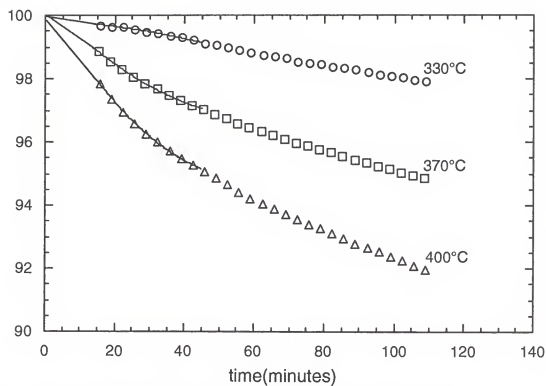


Figure 33. Comparison of IGA data for three different temperatures in air.

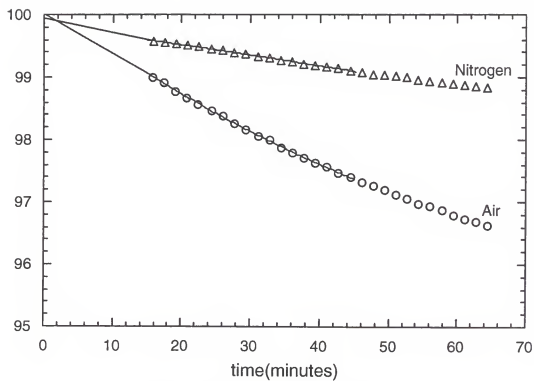


Figure 34. Comparison of IGA data of PEBP for air versus nitrogen atmospheres at 350°C.

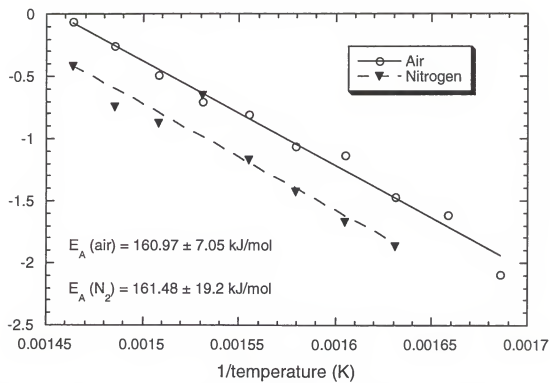


Figure 35. Arrhenius plots for IGA data of PEBP in air and nitrogen atmospheres.

percent of weight loss, the activation energies from the TGA and IGA data are the same. This indicates that the activation energy is independent of the heating profile used to obtain the initial few percent of degradative conversion.

Conclusions

Compounds 1-4 were synthesized. The final monomer (PEBP) was found to melt at 268°C in to a nematic phase and have an onset of thermal degradation >400°C, when heated at 10°C/minute. The thermal degradation temperature is over 50°C higher than that of any of the nBP or nHQ monomers. This is due to the absence of the thermally unstable alkyl chains. The resulting LCT monomer (PEBP) was cured at 350°C in nitrogen. The subsequent crosslinked resin was found to have retained the nematic liquid crystalline ordering of the monomer. The lack of flexible alkyl chains allows the monomer to cure to completion at a high temperature while retaining an ordered structure.

From TGA data, the LCT's high-temperature stability in both air and nitrogen atmospheres at various heating rates was also determined. The thermal stability of the crosslinked resin was found to be higher than other phenylethynyl derived resins. Activation energies for the rates to various percent degradation conversions, in both air and nitrogen, atmospheres were determined. The activation energies determined for the initial few percent of degradation showed little difference between air and nitrogen atmospheres, thus indicating that the activation energies for the initial degradation processes are independent of atmosphere. IGA data also confirms a lack of difference in activation energies for air and nitrogen atmospheres during initial degradation. In addition, the activation energies for the initial few percent of degradative conversion are

the same for both TGA and IGA. For the degradation of the first few percent of material, this indicates independence for the activation energies with respect to the thermal path taken. The high temperature stability indicates that PEBP shows promise as a high temperature matrix material for polymer composites.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

This study focuses on the effects molecular structure has on physical transformations and liquid crystalline phases for acetylene functionalized LCTs. The study consists of three main goals. The basic goals are the synthesis of 13 liquid crystalline monomers (two homologous series of monomers and one fully aromatic monomer), characterization of the monomers during isothermal curing, and thermal stability of the monomers and cured network material.

The synthesis of the acetylene functionalized LCT monomers is accomplished through the use of a modified Heck reaction. Synthesis of monomers with flexible alkyl chains, ranging in length from 3 to 8 carbons, as end-groups is accomplished by coupling an alkynyl-benzoyl chloride with a para-functionalized aromatic diol. The diols are either hydroquinone or biphenol. The fully aromatic monomer is synthesized in the same manner using phenylacetylene and biphenol as the alkyne and diol. The monomers are characterized using cross-polarized optical microscopy, DSC, and TGA. The first observation is that monomers with hydroquinone as the central unit in the mesogen (nHQ monomer series) melt at lower temperatures than the monomers based on biphenol (nBP series). The larger rigid unit allows greater Van der Waals forces and better molecular packing. Upon melting the initial liquid crystalline phase seen for the nHQ series (and the 3BP monomer) is the nematic phase. The 8HQ monomer, however, actually melts to a very short-lived smectic phase. The longer alkyl chains cause the monomer to phase segregate into layers of rigid units and flexible units. All of the nBP monomers with

chain lengths equal to or greater than 4 melt to smectic phases for the same reason. An odd-even effect is seen for the clearing temperatures of monomers in both the nHQ and nBP series. The nHQ monomers have lower transition temperatures than those of the related 1,4-phenylene bis(4'-n-alkoxybenzoates). The curves for the odd-even effects of nHQ and nBP appear to be converging at $n=8$ for both series.

The second goal is the study of the affects of molecular architecture on the liquid crystalline phases and times to gelation during isothermal curing. The gelation times and liquid crystalline phases are determined using parallel plate rheology and cross-polarized optical microscopy. New liquid crystalline-physical-time-temperature-transformation (LCPTTT) diagrams are constructed to elucidate the effects seen due to changes in molecular architecture. The sandwiching of the acetylene functional groups between the mesogen and flexible chain leads to a destabilization of the liquid crystalline phases during curing. While curing in the nematic phase, the monomers begin to clear to an isotropic phase. This is due to a lack of a spacer group between the mesogen and the functional group. Spacer groups typically are used to decouple the mesogen from the growing polymer backbone giving the mesogens more degrees of freedom, thus allowing the mesogens to order with fewer steric interactions. At high enough conversion the LCTs without spacer groups begin to convert back to an ordered phase, assuming curing occurs at low enough temperature to be below the clearing temperature of the network structure. This indicates that both the temperature and the extent of cure control the liquid crystalline phase stability. Upon comparison for the gel times of the nHQ series of monomers at 270°C, a traditionally shaped odd-even effect is evident. This is surprising since the material is cured in the isotropic phase. For the nBP series, an odd-even effect

is also seen, however, the even curve displays independence on gel times with increasing chain length. Both sets of odd-even curves for the gel times of nHQ and nBP converge at $n=8$, the same as the odd-even effects seen for the clearing temperatures of the uncured monomers.

The final goal deals with the thermal stability of a related fully aromatic LCT monomer (PEBP). This allows the comparison of flexible end-groups with rigid end-groups for this family of monomers. As stated earlier, the synthesis of the fully aromatic monomer is similar to that of the flexible chain monomers. In the case of PEBP, the monomer can be cured at 350°C with retention of the nematic liquid crystalline order. The high curing temperature allows quicker curing than for the flexible chain monomers. Upon fully curing, the thermal stability, 5% weight loss with a heating rate of 10°C/minute, of the PEBP material rises to 491°C and 507°C in air and nitrogen respectively. This is due to the network structure allowing recombination of chain ends, caused from chain scission, before fragmentation occurs. From isochronal TGA, the activation energies to reach various degrees of degradative conversion are calculated for both air and nitrogen atmospheres. The activation energies for the initial percents of degradation are the same for both air and nitrogen atmospheres. This indicates independence for the activation energies with respect to atmosphere until around 8%. Isothermal TGA data is also used to calculate activation energies for the PEBP network degradation in air and nitrogen. In this case, the initial degradation rates at various temperatures are calculated and used to determine the activation energies. The activation energies are the same as those for the isochronal TGA studies, ~161 kJ/mol, and also show an independence with respect to atmosphere. These results imply that oxidative

processes are not important for the initial degradation of this material, and that the thermal path taken to achieve the initial degradation has no effect on the activation energy. The thermal stability of PEBP is greater than many other thermosets and moderate with respect to other acetylene end-group materials.

This work is an initial study into the affects of molecular architecture on the liquid crystalline phase stability, physical transformations, and thermal stability of acetylene functionalized liquid crystalline monomers. This study has shown that the liquid crystalline phases for a monomer can be manipulated through the molecular geometry. For example, the addition of terminal flexible groups lowers the melting point, and when long enough will enhance the stability of the smectic phase. Extending the length of the mesogen for a fixed flexible chain length may also induce the smectic phase. In addition, changing of the polarity of the groups directly connected to the mesogen greatly decreases the liquid crystalline phase stability, as seen by the replacing of the alkoxy oxygen with the acetylene group. Finally, fewer alkyl carbons and longer mesogens yield more thermally stable monomers.

The study has also shown that the new LCPTTT diagrams are useful in illustrating the liquid crystalline transitions and physical transformations that occur during an isothermal cure. From the diagrams it is seen that as expected, monomers with increasing terminal chain length take longer to gel; however, an odd-even effect is seen for the time to gelation. Since this was seen for monomers curing in the isotropic phase and in the nematic phase, this may be valid for both liquid crystalline and non-liquid crystalline monomers. Also, without a spacer group to decouple the mesogen from the growing polymer backbone, a loss of molecular ordering initially occurs; however, at a

high enough extent of cure and low enough temperature, the mesogens may begin to reorder and re-attain a liquid crystalline phase. The restoration of the liquid crystalline ordering occurs while the viscosity is becoming greater and the material may vitrify before complete reordering occurs. Addition of spacer groups to decouple the mesogen from the backbone may yield materials with greater molecular order since they will avoid the initial loss of ordering.

Finally, it was found that thermal stability could be tailored through molecular architecture. The thermal stability of the monomers is inversely proportional to flexible chain length, but proportional to mesogenic unit length. Replacement of the flexible chains with phenyl rings yields a monomer with increased melting point, clearing temperature, and thermal stability, but loses the ability to form a smectic phase.

However, there are still many questions remaining with respect to the monomers of this study. The first question that needs to be answered is what is the network structure that is formed for these monomers? This needs to be determined, since if the monomers form different structures this would affect the times to gelation and the liquid crystalline phases. Solid state NMR studies of the resulting network materials would help elucidate the structures. Dynamic NMR studies of the curing systems would also allow elucidation of the cure mechanisms for the network formations. Assuming there is a difference for the different monomers, this would yield a better understanding as to how the molecular architecture changes the cure mechanism for monomers of this type.

Another aspect of interest would be determining the percent monomer conversion needed for gelation for these monomers. It was found that there was a significant amount of liquid crystalline monomer that was not part of the network at gelation. Preliminary

experiments to extract free monomer and oligomer from a gelled 6BP sample showed that upwards of 80% of the initial monomer was extractable. More extensive extraction studies need to be conducted for the various polymers. This may show that a new theory for the critical extent of monomer conversion for homopolymerization of tetra-functional monomers needs to be established.

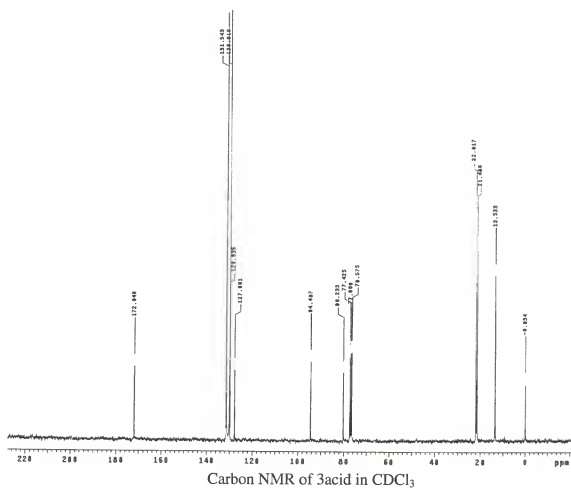
More curing studies at temperatures lower than 250°C might yield data about the temperature dependence of the liquid crystalline phase reemergence during curing. Lower temperature curing will allow examination of kinetics and phase stability for the nBP monomers when cured in the smectic phase (nematic for the nHQ series). Of course, comparison of the networks formed during curing in the more ordered phases may also yield important information.

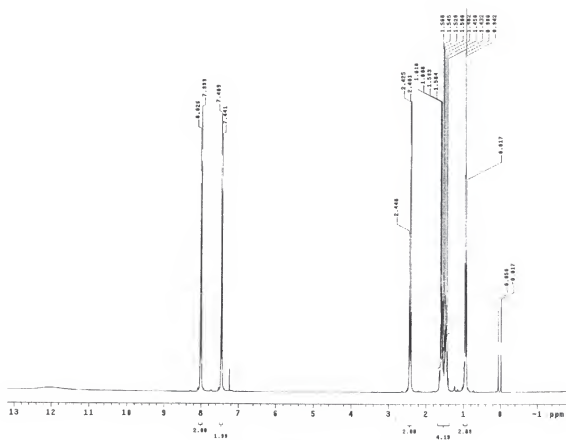
High temperature, wide-angle x-ray scattering studies would yield data about the liquid crystalline phases of the monomers. This would allow confirmation as to the assignment of the liquid crystalline phases. This technique could also yield important data about the liquid crystalline phase transitions that occur during the curing of these materials. For example, it may identify what ordered phase is actually growing during the later stages of curing at the lower temperatures.

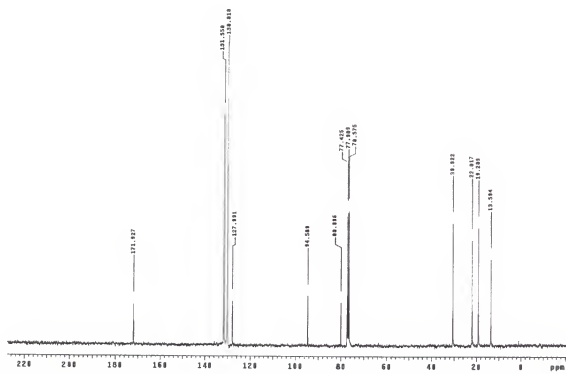
Physical testing, such as tensile testing and fracture analysis, of the cured networks for these materials would yield information as to the affects of chain length and mesogen length on the physical properties, and how manipulation of the molecular architecture will allow tuning of these properties. Longer IGA studies also need to be conducted to determine the long-term thermal stability of these materials.

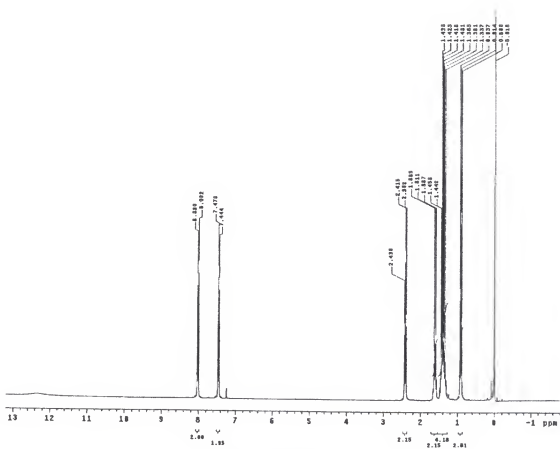
Finally, one of the most important studies that remain to be conducted is that of changing the position of the functional groups. Moving the acetylene group to either the middle or end of the flexible chains will elucidate a couple of very important concepts. First, it will allow the mesogen to be decoupled from the growing network backbone. This may prevent the loss of liquid crystallinity during the initial stages of curing, perhaps retaining more molecular order before vitrification. Second, the analysis of gel times of these new monomers will also allow the determination of functional group reactivity with respect to position. These two studies will allow the tailoring of monomers that will gel in desirable time periods and with the desired amount of molecular order, again allowing the tuning of properties. As described in Appendix B, the synthesis of the precursors for a terminal acetylene functionalized end-group has been attempted. After the precursors are synthesized, the protected 4-bromo-benzoic acid is lithiated and coupled with the protected iodoalkyne. The lithiation and subsequent coupling of the protected precursors was not yet successfully accomplished.

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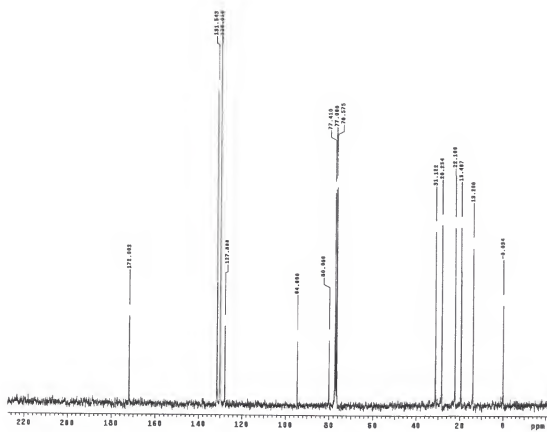


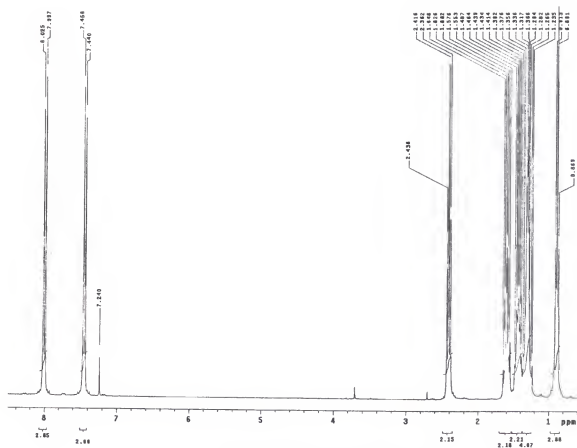
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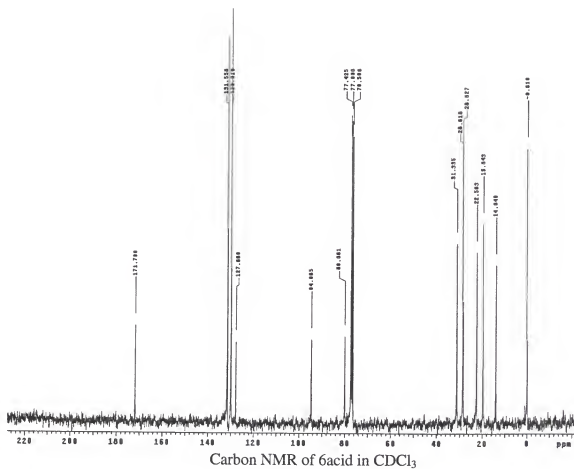
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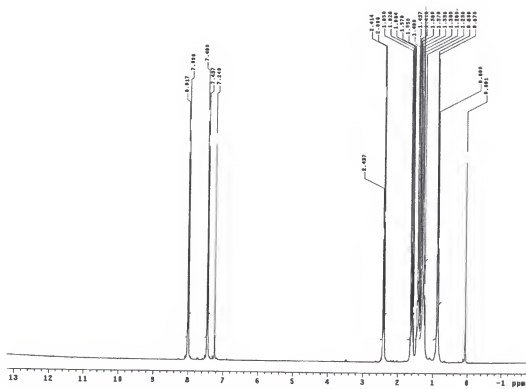


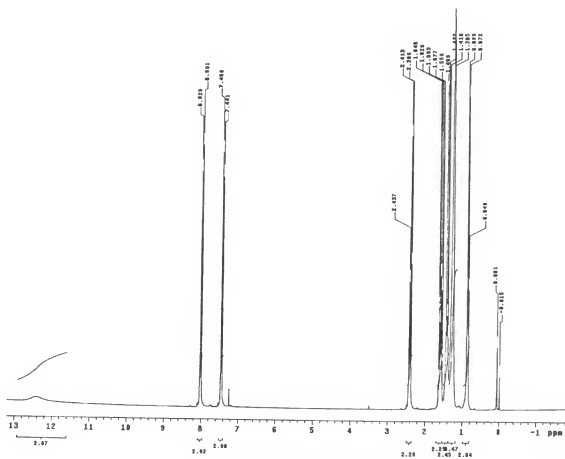
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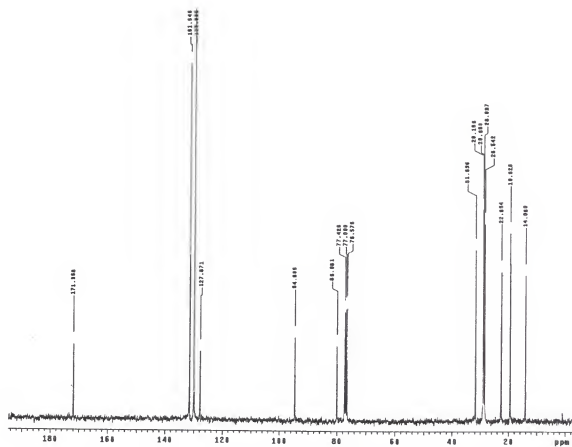
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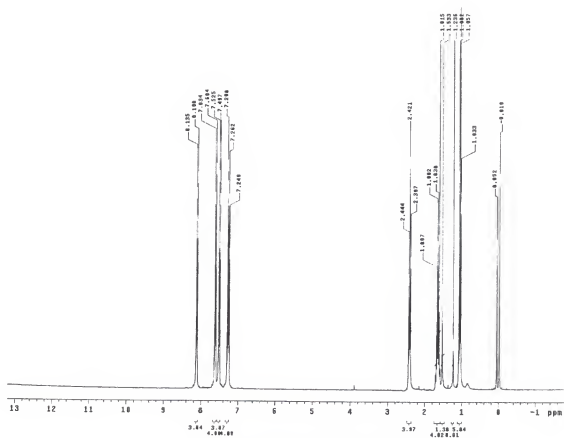
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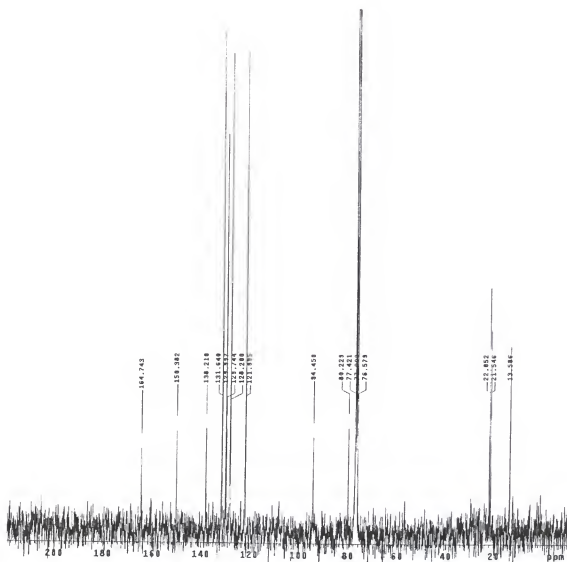


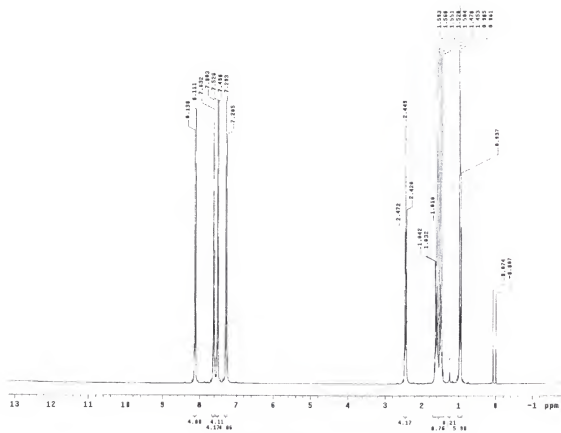
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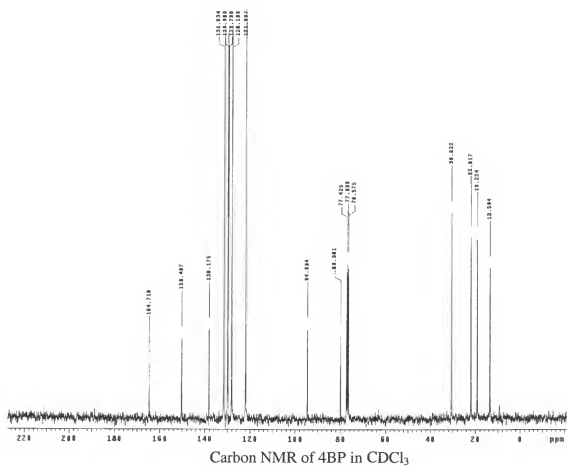
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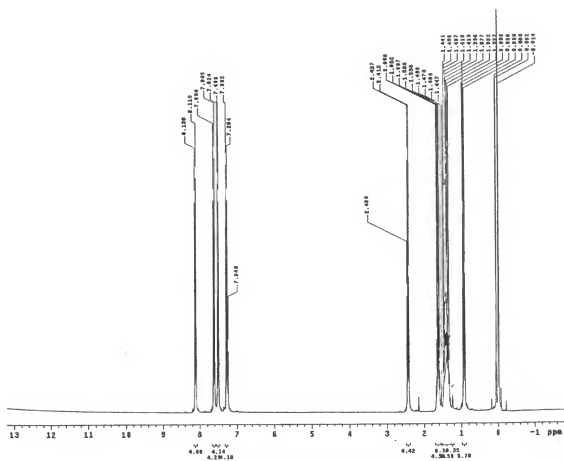
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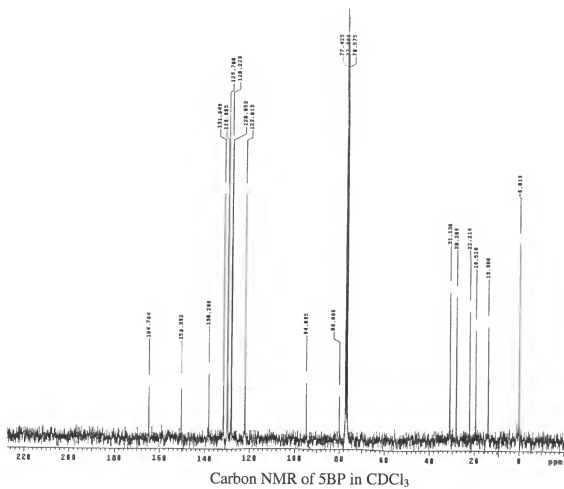
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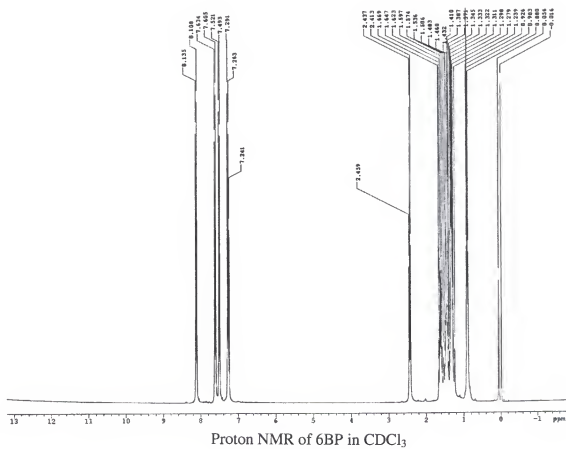
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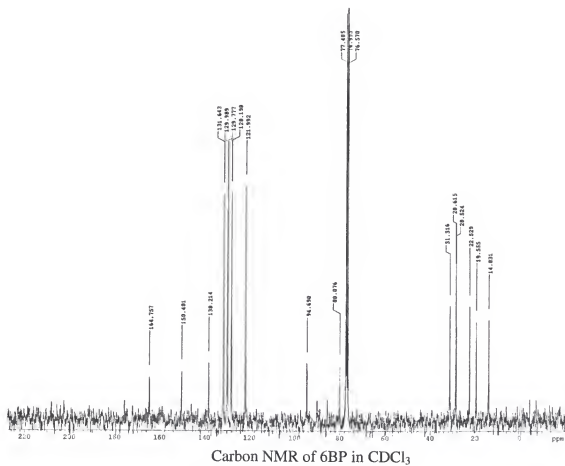
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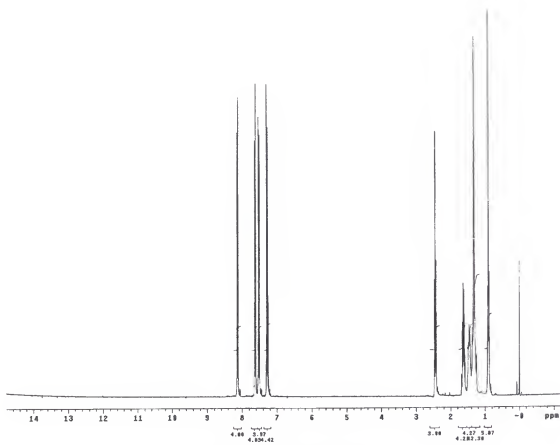


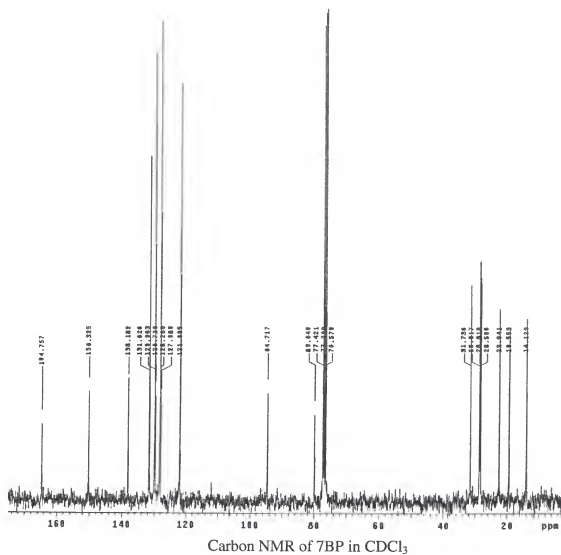
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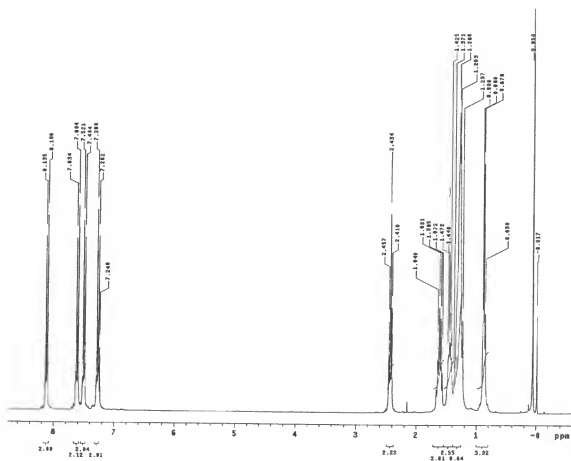


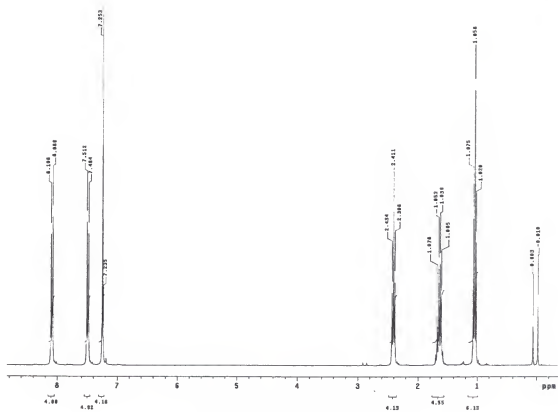


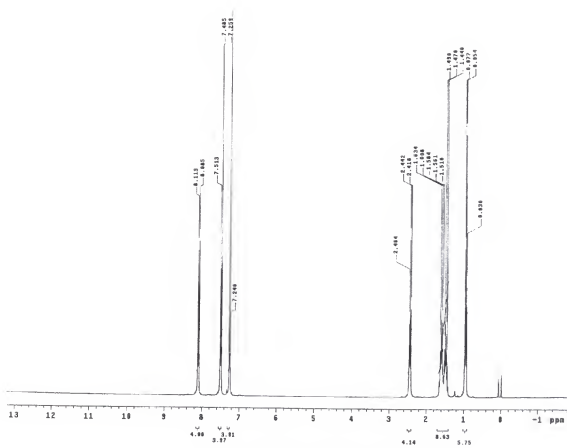


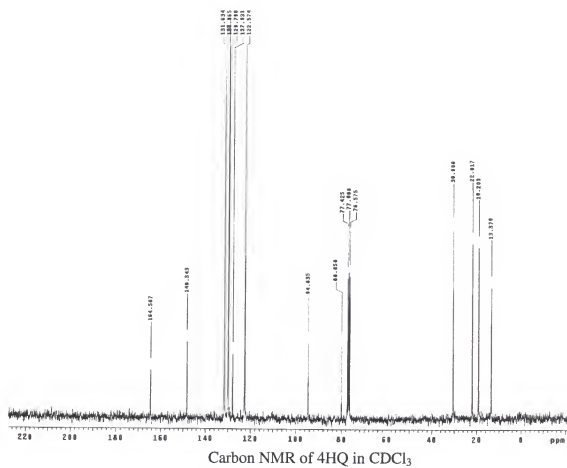
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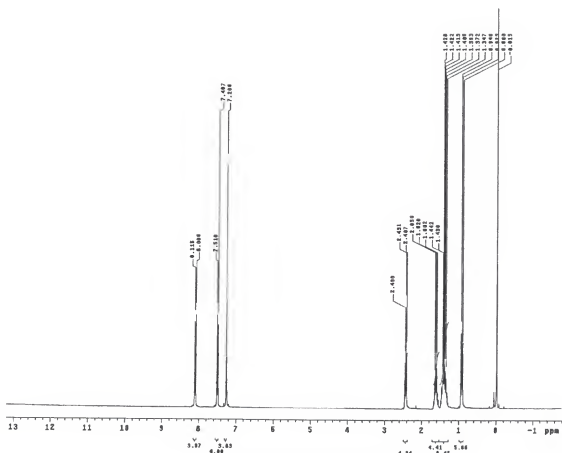


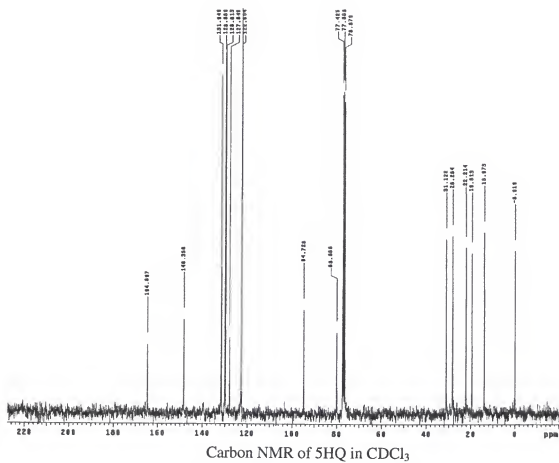
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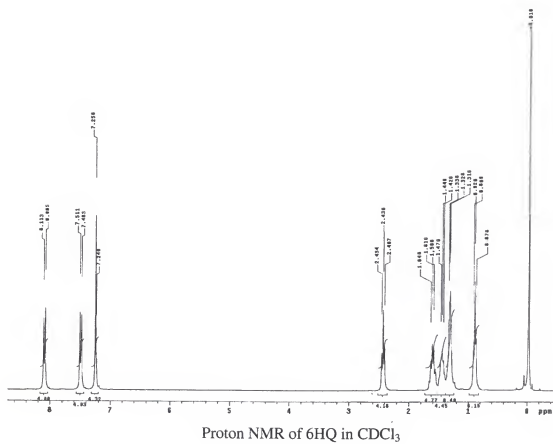
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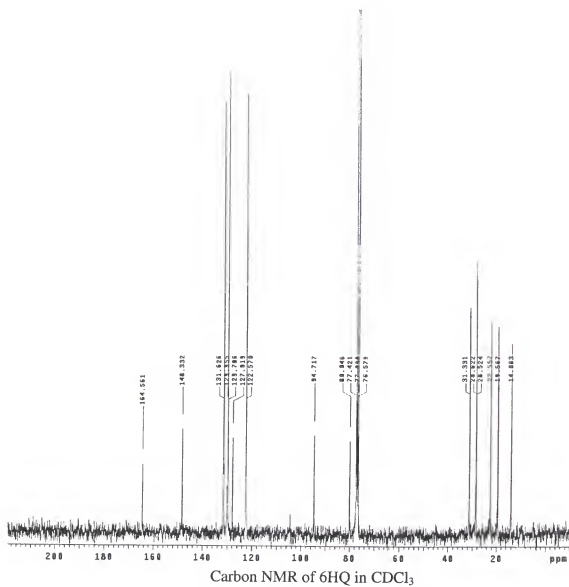
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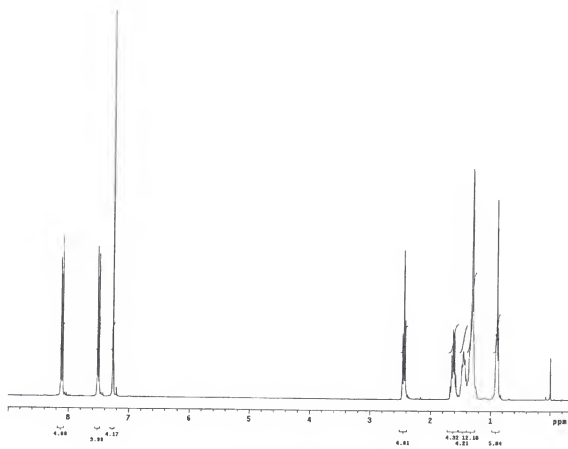


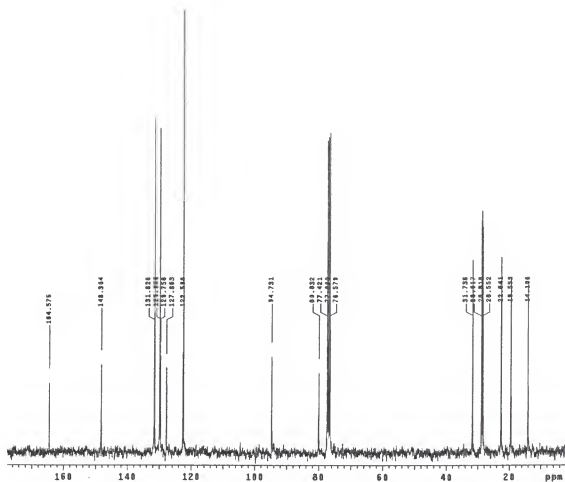


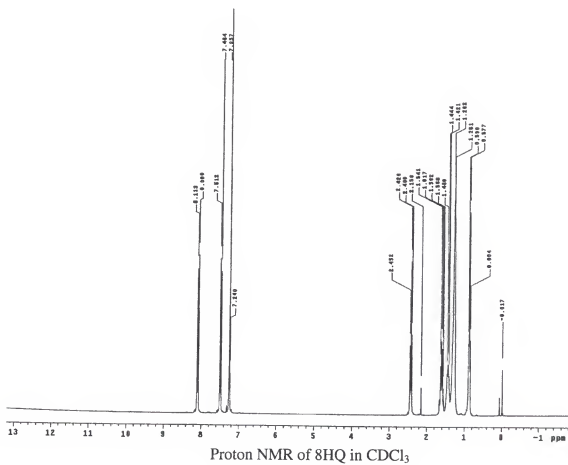


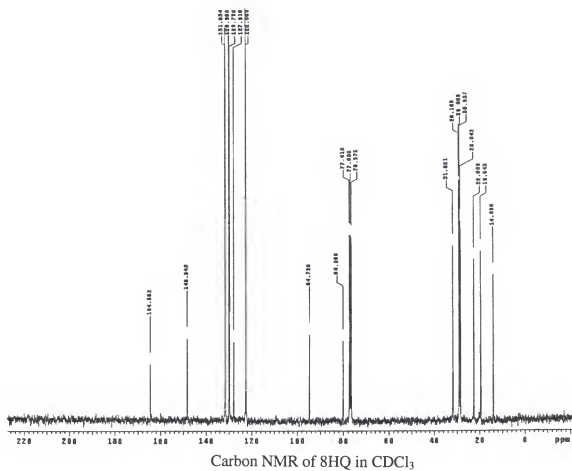




Proton NMR of 7HQ in CDCl₃

Carbon NMR of 7HQ in CDCl₃





APPENDIX B

SYNTHESIS OF TERMINAL ACETYLENE ENDCAPPER

The synthesis of the terminal acetylene endcapper proceeds through the coupling of a protected iodoalkyne and an ortho ester of 2, 6, 7-trioxbicyclo [2. 2. 2] octane (OBO ester) protected 4-bromo benzoic acid. Described in this appendix is the synthesis of the two protected species.

To a 500 mL 3-neck flask with stir-bar, which has been heat-pumped-argon flushed three times, NaI (100 g, 0.5559 mol), dry acetone (100 mL), and 1-chloro-5-trimethylsilyl-4-pentyne (50 g, 0.2861 mol), obtained from GFS Chemicals, were added with stirring. The slurry was brought to reflux for 23 hours. The yellow liquid and white solid slurry was filtered and washed with acetone. The acetone was removed via vacuum. The solution changed to an orange slush, which turned purple when frozen. Upon complete removal of acetone and melting, a yellow liquid with white solid resulted. The slush was dissolved in diethyl ether and filtered. The ether solution was washed twice with aqueous 5% sodium thiosulfate. The ether was then removed via vacuum, yielding the 1-iodo-5-TMS-4-pentyne.

The synthesis of the OBO protected 4-bromobenzoic acid is completed in 2 reactions. The synthesis follows the procedure previously published by Corey.¹¹⁴ First, to a 250 mL 3-neck flask with stir-bar, which has been heat-pumped-argon flushed three times and cooled in an ice bath, pyridine (9.03 mL, 8.828 g, 0.1116 mol), dichloromethane (44 mL), and 3-methyl-3-oxetanemethanol 98% (11.63 g, 11.36 mL,

0.1116 mol) were added with stirring. 4-bromobenzoyl chloride (25 g, 0.1116 mol) was then added. The slurry was diluted with dichloromethane (50 mL) to aid in stirring. The temperature was maintained at 0°C for 5 hours. The cloudy solution was then washed twice with basic water. The organic layer was collected and solvent removed via vacuum. A solid with slight yellow tinge remained.

In the second reaction, to a 250 mL 3-neck flask with stir-bar, which has been heat-pumped-argon flushed three times and cooled to -15°C in an ice/ammonium chloride bath (100 g/25 g), the solid from reaction one and dichloromethane (175 mL) were stirred. Boron trifluoride etherate (3.9598 g, 3.6 mL, 0.0279 mol) was added. The slurry was stirred at -15°C for 9 hours. Triethylamine (11.293 g, 15.6 mL, 0.1116 mol) was then added, and the slurry was allowed to warm to room temperature. The solution was slightly concentrated via vacuum, and then diluted with 3 times the volume of diethyl ether. The ether solution was filtered and washed 3 times with basic water. The ether was then removed via vacuum leaving a thick oil. The oil was dissolved in ethylacetate. Water was added and the organic layer separated. The ethylacetate was then removed via vacuum. The yellow oil was allowed to crystallize over 1.5 days. The crystals were recrystallized in methanol/water. The coupling procedure is also described in the paper by Corey noted above.

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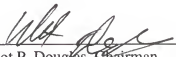
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BIOGRAPHICAL SKETCH

Arthur John Gavrin was born in New York General Hospital, in the year 1969.

He graduated in May 1992 with a Bachelor of Arts degree in Chemistry and English from the University of Rochester. In August 1993, at the end of his first year of graduate studies at the University of Illinois, he met his wife, Jeong-a Ahn. They were married in April 1995. In December of 1995, he graduated with a Master of Science from the Chemistry Department of the University of Illinois. During the summer of 1996, Arthur taught General Chemistry at Montgomery Community College in Maryland. He began to pursue his Ph.D. in Materials Science and Engineering in the fall of 1996. His research has focused on the effects of molecular architecture on liquid crystalline transitions and physical transformations of liquid crystalline thermosets. At 5:34 PM, on November 19, 1999, his son Benjamin was born. Arthur Gavrin will begin a postdoctoral position in the Polymer Science Department at the University of Massachusetts in Amherst in the fall of 2000.

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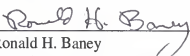
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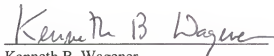
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